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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive Rubber Chemistry and Technology.

(3) Companies and Libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

Officers

Chairman.....STANLEY KRALL, Fisk Rubber Co.
Vice-Chairman.....H. A. WINKELMANN, Philadelphia Rubber Works Co.
Secretary-Treasurer.....H. E. SIMMONS, University of Akron, Akron, Ohio
Executive Committee..A. H. SMITH, N. A. SHEPARD, W. A. GIBBONS, L. B. SEBRELL, IRA WILLIAMS
Sergeant-at-Arms.....E. R. BRIDGWATER

Minutes of the Meeting of the Rubber Division at Atlantic City, New Jersey, September 26 and 27, 1929

In accordance with a vote of the Executive Committee following the regular spring meeting in Columbus, the Rubber Division did not meet with the general society in Minneapolis in September, 1929, but at Atlantic City, September 26–27. The meeting of the Rubber Division was called to order in the Chalfonte-Haddon Hall Hotel, Sept. 26, by Chairman A. H. Smith. The chairman appointed a nominating committee as follows: H. L. Fisher (Chairman), Harold Gray, V. L. Smithers, D. L. Cranor, H. E. Simmons, and the following Resolutions Committee: H. A. Winkelmann (Chairman), C. C. Davis, Carl Frick, and F. W. Stavely.

The following program was given:

C. R. Johnson: "Carbon Black. II. The Role of Oxygen."

A. A. Somerville, J. M. Ball, and W. H. Cope: "The Aging of Vulcanized Rubber under Varying Elongation."

E. Karrer, J. M. Davis, and E. O. Dieterich: "A Simplified Type of Goodrich Plastometer."

W. F. Busse and E. Karrer: "Application of Dunn's Viscosity Equation in the Study of Rubber."

E. O. Dieterich: "A Method for Estimating the Extent of Penetration of Rubber Compounds into Fabric."

V. N. Morris and J. N. Street: "The Effect of Temperature, Pressure, and Humidity on the Permeability of Rubber to Air."

F. L. Kilbourn, Jr.: "Rate of Cure of Reclaimed Rubber. II."

R. H. Gerke: "Thermodynamics of Stretching of Vulcanized Rubber."

W. A. Gibbons: "Flexing Test for Tire Carcass."

J. E. Skane: "Fabrics Used in Rubber Belting."

Report of Physical Testing Committee.

Business Meeting—Election of Officers.

On Friday the business session of the Division was held, at which time the Nominating Committee recommended that it be considered a ruling in the future that the Vice-Chairman is elected with the understanding that he will serve as Chairman the following year. Also the retiring Chairman shall be elected to serve on the Executive Committee the following year and the one receiving next to the highest number of votes for Vice-Chairman shall serve on the Executive

Committee, thus making it necessary to elect but three members to the Executive Committee. This recommendation was approved by vote, at which time the Chairman announced the nominations of the Committee. The balloting elected the following officers for 1929–30: *Chairman*, Stanley Krall; *Vice-Chairman*, H. A. Winkelmann; *Secretary-Treasurer*, H. E. Simmons; *Executive Committee*, A. H. Smith, N. A. Shepard, W. A. Gibbons, L. B. Sebrell, Ira Williams; *Sergeant-at-Arms*, E. R. Bridgwater.

H. A. Winkelmann made a report for the Resolutions Committee, which upon motion was approved.

The Secretary-Treasurer made the following report:

Members of the Division	443
Associate Members	219
Honorary Members	29
Subscribers to "Rubber Chemistry and Technology"	62
Members with dues unpaid for 1929	59
Associate members with unpaid dues	86

By motion this report was approved.

Treasurer's report:

Balance on hand at the meeting in April		$1734.80
Disbursements:		
Translations	$84.23	
Printing	59.75	
Stenographic services	49.99	
Refunds	18.00	
Supplies and postage	12.97	
Mack Printing Co	1543.26	
Rubber Age (N. Y.)	62.88	
India Rubber Publishing Co	122.50	
(Correction made on foreign check—not cashed)	1.97	
Total disbursements	$1955.64	
Deposits since April 1st		553.26
Total deposits		$2288.06
Total disbursements		1955.64
Balance on hand Sept. 25, 1929		$332.42

which by motion was approved.

H. L. Fisher, Chairman of the Papers Committee, submitted a report of the Committee of the Division as follows:

The Papers Committee of the Rubber Division of the American Chemical Society held a meeting at the Chemists' Club, May 28, 1929, and made the following recommendations:

1. That the decisions of the Executive Commttee regarding papers to be presented before the Divsion be rigidly enforced, with the exception of that part which reads, "That the titles of the papers be in the hands of the Secretary three months prior to the meeting." It is recommended that this part be rescinded. These decisions are found in the minutes printed on page viii of the April, 1928, number of RUBBER CHEMISTRY AND TECHNOLOGY (Vol. I, No. 1) and, without the part just mentioned, are as follows:

A. "That the papers be in the hands of the Secretary six weeks prior to the meeting."

B. "That the Chairman appoint two or three men to act as reviewers for each paper presented to the Division and to lead in the discussion of the paper, and that the reviewers give the Secretary the number of minutes that should be allotted on the program for the respective papers."

2. That the names of those appointed to review and discuss each paper be published, together with their discussion.

3. That the author may designate the time he thinks necessary for the presentation of his paper, and that he be notified of the time allotted to him.

4. That the author send in an abstract of not over 200 words along with his manuscript and that all abstracts be mimeographed and sent to each member of the Rubber Division a reasonable time before the meeting.

5. That a paper should usually consist of the following parts:
   A. Synopsis
   B. Brief introduction
   C. Main body, including experimental work
   D. Conclusions
   E. Bibliography.

6. That, in the presentation at a meeting, the author should never read his complete paper. He should use a comprehensive abridgment, and carefully think over his method of presentation beforehand. Properly made slides or charts are most helpful and, when discussing them, the speaker should talk to his audience, not to the screen.

7. That the author should observe the following in the make-up of the slides:
   A. Too much should not be put on one slide
   B. All curves should be distinctly drawn
   C. Letters and figures should be large enough when on the screen to be legible from the rear of a 100 ft. room
   D. Slides should be numbered.

8. That charts, curves, and tables for publication should conform with the recommendations on these matters given in the artiele in *Industrial and Engineering Chemistry*, **19**, 755 (1927). Authors are reminded of the fact that in all American Chemical Society publications the metric system of units must be used; and that the English system may be used in addition. Which upon motion was approved by the Division.

Following this the Division adjourned its meeting.

H. E. Simmons, *Secretary-Treasurer*

Minutes of the Meeting of the Executive Committee, September 27, 1929

The newly elected Chairman of the Division, Stanley Krall, called a meeting of the newly elected officers of the Division immediately upon the adjournment of the Division, members present being: Stanley Krall, H. A. Winkelmann, W. A. Gibbons, A. H. Smith, Ira Williams, E. R. Bridgwater, H. E. Simmons.

By motion of the Executive Committee it was decided that the rules which apply to membership in the American Chemical Society should also apply to membership in the Rubber Division, therefore, any one whose dues for 1930 are not paid on or before February 1 will be dropped from the mailing list and thus be removed from the mailing list of Rubber Chemistry and Technology. After some discussion it was moved that the programs of the different groups of the Rubber Division be submitted in advance to the Executive Committee of the Rubber Division for their approval.

Because of the increasing duties in the office of the Secretary-Treasurer it was voted that the Secretary be allotted $10.00 per month for stenographic services, said amount to be paid in four equal installments of $30.00 each.

It was also voted that the expenses of the Secretary-Treasurer of the Division in attending meetings be paid by the Division, this to go into effect with the Atlantic City Meeting.

Upon motion, the Committee adjourned to meet again at the call of the Chairman.

H. E. SIMMONS, *Secretary-Treasurer*

New Books and Other Publications

The Reclaiming of Rubber Products. Paul Bary. 144 pages, 40 illustrations, 16 tables. In linen, 30 francs. L'Édition Technique, Paris, Avenue Jean Jaurés, 61. 1928.

By his lucid style and clarity of presentation in this small book, the French author, who is so well known through his numerous works in the field of rubber in general and in the colloid chemistry of rubber in particular, has made a noteworthy contribution to our present knowledge of reclaiming. The book is divided into the following chapters: vulcanized scrap, the theory of reclaiming, reclaiming by heat and alkali, the production of reclaimed rubber by the caustic soda process, complete reclaiming, reclaimed rubbers and their utilization. Each chapter contains exhaustive information on the literature of the subject. The references to the numerous patents on reclaiming are of particular interest. The book gives valuable hints to all who are or wish to be concerned with reclaiming, and to all who use reclaimed rubber in rubber mixings, and it will doubtless be instrumental in correcting the false ideas which prevail even today on the nature and value of reclaimed rubber. [Hauser in *Kautschuk*.]

Déchets et Régénérés. A new monthly review devoted exclusively to rubber scrap and reclaimed rubber. Published at 16 Rue des Saussaies, Paris. First number appeared June, 1929. Foreign subscription, 30 francs.

The character of this new publication may be judged by quoting from the editorial in the first issue. "It was considered that it would be useful to every technologist and industrialist concerned with the manufacture of rubber goods to receive regularly, through a professional review, information covering all progress in the scrap and reclaiming industries. Original articles, reviews of foreign publications, statistics, formulas, commercial data will be furnished by specialists and will contribute to some extent to facilitate the work of the manufacturer. By publishing well-tried processes and formulas the aim is to foster economy of manufacture and to aid in the advance of the industry." [From *Déchets et Régénérés*.]

Rubber Research Scheme (Ceylon). This is the seventh report of the Executive Committee to members and includes proceedings of the year 1928, accounts of the various committee activities, reports by the chemist, physiological botanist, mycologist, and that of the London Advisory Committee, and concludes with list of members, subscribers, and financial report. [From *India Rubber World*.]

Crepe Rolling is Bulletin No. 50 of the Rubber Research Scheme (Ceylon), by its chemist, T. E. H. O'Brien, M.Sc., A. I. C., Peradeniya, March, 1929. This little paper booklet of 30 pages contains a fund of information on crepe rolling, amplified by tests, tables, and formulas. There is also a brief bibliography. [From *India Rubber World*.]

British Colonial Office Reports on the Rubber Situation. Trade Information Bulletin No. 603, published by the Department of Commerce, Bureau of Foreign and Domestic Commerce, United States Government Printing Office, Washington, D. C., was compiled by E. G. Holt, Chief, Rubber Division. This 40-page paper booklet contains the original report of the Colonial Office (Stevenson) Committee, issued in May, 1922; the supplemental report of the Colonial Office Committee, issued in October, 1922; the edited statement of the Colonial Secretary in the

House of Commons in April, 1928; and the report of the Under-Secretary of State for the Colonies, issued in December, 1928. [From *India Rubber World.*]

26th Annual Report of the Bureau of Science, Philippine Islands. Published by the Bureau of Printing, P. I. 1929. 81 pp.

A survey of the diseases of Hevea rubber in Mindanao and Basilan, mentioned in this report to the Department of Agriculture and Natural Resources of the Philippines, indicates that the plantations, although harboring several of the major diseases, are in general in a thrifty condition as the result of close inspection and early eradication of minor outbreaks. [From *The Rubber Age* of New York.]

The Rubber Exchange of New York, Inc., By-Laws and Rules has been issued recently in a new edition by the Rubber Exchange. It is a handsome book in loose-leaf form, bound in composition rubber covers, $5^3/_4$ by $7^3/_4$ inches. Its contents include: Officers, Governors, Committee Members; Charter; By-Laws; Trading Rules; Delivery Rules; Commission Law Rules; Rules Governing Arbitration; Index; and Clearing House By-Laws and Rules.

Tubing, Rubber; Hose, Water, and Wash Deck; and **Hose, Suction, Water (Smooth Bore)** are United States Government Master Specifications 39*c*, 48*c*, and 50*b*, respectively. These eight-page paper pamphlets are issued by the U. S. Department of Commerce, Bureau of Standards, Washington, D. C., in accordance with the revision promulgated by the Federal Specifications Board on December 8, 1928, and published by the Bureau of Standards. The contents deal with general specifications, grades, material, and workmanship, general requirements, detail requirements, method of test, and analysis or inspection and sampling, packing, and marking of shipments, and notes. [From *India Rubber World.*]

Quality of the Cotton Spun in the United States (Year Ending July 31, 1928). A preliminary report by Peter M. Strang, Senior Cotton Technologist of the Department of Agriculture, Bureau of Agricultural Economics, Division of Cotton Marketing, Washington, D. C., June, 1929. This 16-page paper booklet contains a fund of information, supplemented by several tables, treating of the production and consumption of cotton. Special reference is made to the tire industry. [From *India Rubber World.*]

Facts and Figures of the Automobile Industry, 1929 edition, is issued by the National Automobile Chamber of Commerce, 366 Madison Avenue, New York, N. Y. As usual this booklet contains much interesting data regarding the automobile industry. The information is supplemented by tables, charts, and graphs. Paper, $5^7/_8$ by $8^5/_8$ inches. 96 pages. [From *India Rubber World.*]

Tire Table of Balloon Tires and the Cars That Use Them. A circular issued by National Rubber Machinery Co., Akron, O., giving sizes of tires used in 1925–26–27–28–29, and the make of car using them. This is a valuable tabulation. [From *India Rubber World.*]

The RMA Manual of Tire Repairing. Published by the Rubber Manufacturers Association, Inc., 250 West 57th Street, New York City. 1929. 64 pp.

Tire manufacturers some years ago realized the advisability of coöperating to give the tire repairman the benefit of their combined experience and research work. In this, the third edition of this handbook published in as many years, several improvements developed by the various companies have been incorporated. The manual is being distributed to repairmen throughout the country by the Tire Accessories and Repair Materials Committee of the Association. [From *The Rubber Age* of New York.]

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the July 10 and 20, August 10 and 20, and September 10 and 20, 1929, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial, and trade journals throughout the world.

New developments in the rubber industry. The Peachey process. F. JACOBS. *Caoutchouc & gutta-percha* **26,** 14,506–9(1929).—A detailed description of the process and its latest developments. C. C. DAVIS

Making rubber goods of latex by electrodeposition. PAUL KLEIN. *Rubber Chem. & Technol.* **2,** 278–84(1929).—See *C. A.* **23,** 2067. C. C. DAVIS

The chemical constitution and the mechanical properties of rubber. LOTHAR HOCK AND GUIDO FROMANDI. Phys.-Chem. Inst., Univ. Giessen and Gummiwarenfabrik, Poppe & Co. *Kautschuk* **5,** 81–2(1929).—When synthetic isoprene-rubbers are treated electrically so that their viscosity, softening temp., mol. wt. and I no. increase to values similar to those of plantation rubber (cf. F., *C. A.* **23,** 1009, 2323), their phys. characteristics also approach closely those of natural rubber. Moreover, a decrease in these consts. through elec. treatment of a high-grade natural rubber is accompanied by a loss of the most desirable properties of the rubber. This suggested that the poorer phys. characteristics of certain lower-grade com. rubbers might be assocd. with a lower I no., *i. e.*, a lower degree of chem. unsatn. Purified rubber (by the Pummerer method) gave almost the theoretical I no. (372.8). Smoked sheet with 3.2% acetone ext. and 0.4% ash had an I no. of 348. Kongo rubber with 5.9% acetone extn. and 1.7% ash had an I no. of 329. In the latter case the acetone-sol. part had an I no. of 24, so that with 5.9% ext., 1.4 units were to be subtracted from the I no. of the rubber, giving 327.6 for the I no. of the rubber hydrocarbon. Dissolved in C_6H_6, filtered, pptd. twice with acetone and once with EtOH, and dried *in vacuo*, the I no. increased to 351.4. The same results were obtained with a Peruvian rubber. This treatment did not remove all impurities, and since the I no. approached so much nearer the theoretical value, it is doubtful whether there is any relation between the poorer phys. properties of the Congo rubber and its degree of unsatn., particularly since the elastic properties of rubber depend upon its colloidal state as well as upon its chem. constitution. This is also still more probable when the rubber is mixed with fillers, because the quality then depends upon the surface energy between the rubber and filler, which is governed by the phys. and chem. state of the rubber and the presence of non-rubber components. C. C. DAVIS

Titanium dioxide in the rubber industry. RUDOLF DITMAR. *Kautschuk* **5,** 79–81(1929).—The characteristics and behavior of TiO_2 as a rubber compounding ingredient are described. Among the properties which may be of importance are its ability to soften rubber notably during milling and the limitations in the choice of accelerator to obtain a strictly white vulcanizate when it is used as the only white pigment. C. C. DAVIS

The effect of mixtures of crude ozocerite and "Agerite" on the aging of rubber mixtures. F. KIRCHHOF. *Caoutchouc & gutta-percha* **26,** 14,501–3(1929).—Ozocerite and "Agerite" fused together to a homogeneous mixt. give a product which combines the antioxidant and plasticizing properties of each component. Excellent results were obtained with a mixt. contg. 3–5% "Agerite" in ozocerite. Tests of vulcanized rubber which deteriorated rapidly with no antioxidant showed that its aging, judged by the deterioration of its phys. properties in air at 52° and at 75°, could be greatly improved by the addn. of the mixt. described, even when only enough of the mixt. was added to furnish 0.1% "Agerite" (by wt. of the rubber mixt.). This antioxidant effect was disproportionately great, for the 0.1% "Agerite" added in this form gave the same

protection as 0.5% added alone, *i. e.*, with ozocerite mixts. the same effect can be obtained as with 5 times as much Agerite added in the ordinary way. Photographic observations with ultra-violet light of the deteriorated samples showed that O penetrated less into the interior of the samples contg. ozocerite-Agerite than into those contg. none and the deterioration in phys. properties was proportional to this penetration. C. C. D.

The thermochemistry of rubber. SIEGFRIED BOSTRÖM. Univ. Giessen. *Rubber Chem. & Technol.* **2**, 259–74(1929).—English version of *C. A.* **22**, 4271. C. C. DAVIS

A thermodynamic theory of rubber fillers. LOTHAR HOCK. Univ. Giessen. *Rubber Chem. & Technol.* **2**, 275–7(1929).—An English version of *Z. Elektrochem.* **34**, 662(1928) (*C. A.* **23**, 2321). C. C. DAVIS

Pigment reënforcement. R. W. LUNN. *Trans. Inst. Rubber Ind.* **4**, 396–412 (1929).—In the present investigation energy is chosen as the criterion of reënforcement. In the past, pigments have been compared by the resilient energy values of rubber mixts. contg. equal vols. of the pigments, but in the present paper the total energy is analyzed into that pertaining to the rubber and that to the pigment. Expressed mathematically, if E_A is the total energy of a mixt. contg. a pigment A, e_R the energy of the rubber component, and e_A the energy from x vols. of A, then $E_A = e_R + e_A$, and e_A/x is the energy from 1 unit vol. of pigment, this e_A/x value being a characteristic of the pigment. The object of the expts. was to det. e_A/x at various concns. of pigment and at various elongations up to rupture. If x vols. of pigment are added to a cube contg. 100 vols. of rubber, the new cube is $(1 + x/100)$ times as large. Furthermore, if it is assumed that the pigment concentrates at 1 end of the enlarged cube, when this cube is elongated, the rubber and pigment elongate to the same degree, *e. g.*, when the cube is elongated 100%, both rubber and pigment elongate 100%. There are objections to this analysis, but the energy value of the pigment independent of the energy value of the rubber component may be readily detd. up to the breaking point. Pptd. $BaSO_4$, ZnO, Thermatomic black and gas black were studied on this basis. An org. accelerator was not used in the base mixt., chiefly because of the influence of the pigments on it. The base mixt. was: rubber 100, S 3 and PbO 10.3. The rubber was plasticized to an extreme degree to minimize the variations in milling necessary with the different pigments. To the base mixt. were added various proportions of the different pigments, and the resulting mixts. were vulcanized for a time and at a temp. which corresponded to that cure which gave the max. resilient energy for the base mixt. The results are recorded in graphical form, including the change in plasticity of rubber on mastication, the tensile strength, elongation, stiffness and energy of the base mixt. cured to different degrees, variations in the energy with concn. of the pigments, total energy-elongation relations, concn. of pigment-elongation relations, pigment energy per unit vol. of pigment, and the change of pigment energy per unit vol. with the concn. These results admit of certain general conclusions. Up to a high concn. C black increased the total energy, ZnO and Thermatomic black increased it much less and the maxima were at far lower concns., and pptd. $BaSO_4$ increased it still less so, with its max. at a still lower concn. A comparison of the total energies at elongations below the breaking point shows that up to 50 vols. concn., $BaSO_4$ behaved like Thermatomic black and ZnO, while the C black showed much higher total energy values. With data on the base mixt. and on the loaded mixts., it was possible to calc. the energy due to the pigment, a vol. correction factor being used so that each mixt. was based on a unit vol. of rubber. The resulting curves of the pigments were similar to those showing total energy as a function of elongation. Finally the pigment energies per unit vol. of pigment are expressed graphically. In no case was there a sharp change in the mechanism of reënforcement as the proportion of pigment increased, the ultimate reënforcement per unit vol. declining progressively with increase in concn., with no evidence of agglomeration or of diln. With gas black and Thermatomic black, the reënforcement per unit vol. at definite elongations increased with increase in the concn., the effect being more marked with gas black. The reënforcement per unit vol. by ZnO increased less markedly above 10 vols. concn., while with $BaSO_4$ above 20 vols. concn. it reached an approx. const. value at each elongation. Natural barytes would probably have behaved differently. The results show the sp. reënforcing power of the pigments at various concns. and elongations. The sp. reënforcing power of gas black and of Thermatomic black increased with the concn. and the elongation; with ZnO it increased in the same way but to a lesser degree, while the sp. reënforcing power of $BaSO_4$ reached a const. value for each concn. and elongation. This suggests that there may be pigments which, beyond a crit. point, should exhibit a progressively diminishing reënforcing power. Curves of the ultimate energy values as the energy per unit vol. concn. of pigment show a trend toward 0 energy with increase of concn., suggesting that the

pigment energy may become 0, *i. e.*, act as a diluent, but that neg. reënforcement does not occur, where the energy of the rubber component is diminished. The curves approach closely from 50 vol. concn. upwards, indicating that at high concns. no pigment has any notable advantage over any other pigment from the point of view of the energy imparted to a rubber mixt. C. C. DAVIS

The coloring of rubber. W. J. S. NAUNTON. *J. Soc. Dyers and Colourists* **45,** 31–5(1929).—See *C. A.* **22,** 4875; **23,** 2068. T. G. HAWLEY, JR.

The behavior of Prussian blue and some other ferrocyanides in rubber. J. R. SCOTT. *Trans. Inst. Rubber Ind.* **4,** 374–95(1929).—An elaboration of *C. A.* **22,** 2683. Preliminary expts. on *plasticity*, the results of which are to be reported later in greater detail, indicate that uncured rubber mixts. exhibit plastic flow so as to conform at least in an approx. way to the law: $F = a(vc/s + f)$, where F is the shearing force, a the area between parallel surfaces, v the relative velocity of the surfaces, c the consistency, s the distance between surfaces and f the friction or yield value. C. C. D.

Industrial applications of a terpene product. ÉMILE ROUXEVILLE. *Rev. gén. caoutchouc* **6,** No. 50, 9–12(1929).—The terpene product which has already been described as a valuable reclaiming agent (cf. *C. A.* **23,** 1775) has a wide industrial application, *e. g.*, in agglomerating ground cork, as an adjunct in the prepn. of rubber-leather mixts., impregnating cotton fabrics to improve the quality of ebonite, etc. C. C. D.

Isoprene and rubber. XIV. Degradation of rubber and gutta-percha. H. STAUDINGER AND H. F. BONDY. Univ. Freiburg. *Ann.* **468,** 1–57(1929); cf. *C. A.* **23,** 2847.—An investigation is made of the degradation of rubber and gutta-percha by heat. The materials used were a raw rubber contg. about 5% protein, rubber purified by Pummerer's method and gutta-percha obtained from a leaf gutta-percha, the CCl_4 soln. being centrifuged from impurities, filtered and pptd. with MeOH. The viscosity of a C_6H_6 or PhMe soln. of gutta-percha was not affected by boiling but $C_6H_4Me_2$ or $C_{10}H_{12}$ solns. of this substance, as well as all 4 solns. of raw and purified rubber, underwent an appreciable change of viscosity, the change being the greater, the higher the b. p. of the soln. It follows that the rubber undergoes degradation at fairly low temps., whereas gutta-percha withstands higher temps. Degradation of rubber in boiling $C_6H_4Me_2$ produces gummy products, mol. wt. about 4200, while gutta-percha gives powdery substances, mol. wt. about 2500. Both products are regarded as being lower members of the 2 different series of which rubber and gutta-percha, resp., are complex members. In boiling $C_{10}H_{12}$, further degradation does not take place, although cyclization of the open-chain residues takes place to some extent. It is only at temps. above 300° that both decomp. to give identical products. The degradation of raw rubber appears to be inhibited somewhat by the presence of the protein at temps. up to 142°, but at higher temps. it follows a course similar to that observed with pure rubber. (With E. GEIGER.) The pyrogenic decompn. of gutta-percha begins at 285–90° and 11 mm., becomes vigorous at 300–15° and then ceases. Sixty g. of pure gutta-percha, heated 7 hrs. at 300–10° and 11 mm., gives 57% distillate and 40% residue; the latter is *a polycyclo-gutta-percha* $(C_5H_8)x$, mol. wt. in freezing C_6H_6, 1950, which contains 1 double bond (Br titration). Catalytic reduction with H and Ni gives a *hydro deriv.* $(C_{25}H_{42})_x$, mol. wt., 1930, n_D^{16} 1.5238. Raw rubber in boiling $C_{10}H_{12}$ with HCl gives a *cyclorubber*, mol. wt. 2500, liquefying at about 123°, while gutta-percha gives a *cyclo-gutta-percha* indistinguishable from the rubber product. At lower temps., however, the 2 give different cyclization products. The *cyclorubbers* obtained in boiling $C_6H_4Me_2$ and PhMe have mol. wts. 4000–12,900 and 14,000, resp. The *cyclogutta-perchas* obtained in boiling $C_6H_4Me_2$, PhMe and C_6H_6 have mol. wts. 2600–8100, 10,000 and about 8500, resp. Cyclization in PhMe at 20° gives different products with very high mol. wts. The heat-degradation products of rubber and gutta-percha are hemicolloids, mixts. of polyprenes with an av. mol. wt. of 10,000, which are relatively stable. This explains the considerable soly. of the products, the fact that the mol. wt. does not vary with concn. and the fact that the viscosities of solns. of the products are roughly proportional to the concn. Rubber, on the other hand, is a eucolloid, consisting of a mixt. of polyprenes having an av. mol. wt. of 100,000. Even a slight temp. elevation causes degradation. The macro-mol. is the colloid particle. The structures of the 2 compds. are discussed. Rubber contains about 1000 isoprene residues covalently united, and may be a *trans*-compd. The mol. of gutta-percha is smaller (about 300–500 isoprene residues), is more sym. and is possibly a *cis*-compd. C. J. WEST

British standard specification for friction surface rubber transmission belting. ANON. *Brit. Eng. Standards Assoc.* (London) No. **351,** 13 pp.(1929).—Specifications for construction, fabric, joints, freedom from defects, tolerances on width. Methods of testing for elongation, strength of fabric, adhesion and seam strip are given. E. I. S.

Manufacture of rubberized cloth and attendant cloth dyeing problems. S. G

BYAM. *Am. Dyestuff Reptr.* **18,** 15–23(1929).—Dry heat curing is considered most satisfactory for rubberized fabrics. Testing of rubberized fabrics is discussed. Tentative fabric specifications for rubberized cloth are given. T. G. HAWLEY, JR.

The nature of vulcanization. W. H. STEVENS. *J. Soc. Chem. Ind.* **48,** 60–2T (1929); cf. *C. A.* **22,** 1703.—A crit. review and discussion of exptl. facts known about vulcanization leads to the conclusion that vulcanization is the phys. manifestation of the chem. combination of rubber with S (or other elements), the mechanism of which is a reënforcement by the resultant S reaction product, with or without coexistent sorption. Thirty-five references are included. C. C. DAVIS

Vulcanization and the structure of rubber. HEINRICH LOEWEN. *Kautschuk* **5,** 77–9(1929).—A criticism of various features of an article by Lindmayer (cf. *C. A.* **23,** 2323). C. C. DAVIS

The tackiness of unvulcanized rubber. T. L. GARNER. *Trans. Inst. Rubber Ind.* **4,** 413–23(1929).—The expts. are concerned chiefly with the *action of light on raw rubber* and on rubber to which has been added a small proportion by as little milling as possible, and are in part an amplification of previous work by other investigators. The tackiness of the samples was judged by their viscosities, a *viscometer* of the Ostwald type being used. In ordinary cases of exposure of raw rubber to air and light, tackiness and oxidation proceed concurrently, but it was possible to reduce the viscosity of a rubber soln. in the absence of O by exposure to ultra-violet light. Such a soln. gave on evapn. a depolymerized rubber which readily absorbed O. Introduction of a small quantity of O into a tube contg. rubber in an atm. of N gave on exposure a rubber apparently as tacky as if exposed to air. The only difference was that part of the rubber was rendered insol. The action of light was in part polymerization and in part depolymerization, the extent of each depending upon the conditions. The presence of O was necessary for the formation of a tacky film, thus confirming expts. by Fry and Porritt (cf. *C. A.* **22,** 4870). Little change in the soln. viscosity of rubber or its soln. took place when heated to 40° in the absence of light. Under the conditions of the expts., no insol. rubber was obtained by exposing solns. of uncompounded rubber in air, but in inert gases the formation of insol. rubber of the polymerized O-free type of Asano (cf. *C. A.* **19,** 3616) was observed to increase with the time of exposure. The insol. rubber, formed when rubber protected by the addn. of an antioxidant was exposed to light, did not appear to be of this type, but rather the transparent oxidized rubber obtained by Asano. At the same time, the rate of oxidation, judged by the increase in acetone ext., did not progress to the same extent as with unprotected raw rubber. The protection against tackiness afforded by antioxidants is apparently unrelated to their value in preventing changes resulting from oxidation. Of importance in the technical use of antioxidants is the fact that they protect rubber in such a way that they prevent to some extent depolymerization and changes due to oxidation, thereby promoting the formation of an insol. polymerized rubber. This was not manifest in ordinary exposure. Thus an insol. layer of rubber was formed on the surface of the exposed rubber and the tackiness was destroyed. Consequently the use of much antioxidant in a rubber mixt. which must remain tacky where exposed in light in a factory for some time is inadvisable. On exposure to light, rubber mixts. contg. 1% antioxidant lost their surface tackiness much more rapidly than the corresponding mixts. contg. no antioxidant, the surfaces of the mixts. contg. antioxidant becoming dry and hard. The results suggest a *theory of tackiness*. When raw rubber is masticated, part of the globules burst and simultaneously the rubber hydrocarbon depolymerizes, which reduces the soln. viscosity. The tackiness of unmasticated rubber is due to the action of O upon the depolymerized hydrocarbon, and this tackiness cannot appear until depolymerization has occurred. Thus, on exposure of unmasticated rubber, the surface layer must first be depolymerized and then oxidized. In protecting rubber from depolymerization and subsequent oxidation, antioxidants permit the polymerizing action of light to become the predominant effect. Accordingly in a tacky rubber, repolymerization of the depolymerized-oxidized layer occurs to some extent, and the loss of tackiness is proportional to the extent of polymerization. In ordinary masticated rubber, the depolymerized-oxidized rubber is distributed throughout the mass, but in certain cases only the surface is affected. Tackiness is destroyed by substances which migrate to the surface and form greasy films, *e. g.*, stearic acid, or by substances which in any way promote the polymerizing action of light. Therefore, where tackiness is desired, conditions such as those described which favor this tendency must be eliminated. C. C. DAVIS

Exploitation of Euphorbia in South Africa: examination of the rosin and rubber. W. SPOON AND M. VAN ROYEN. *Ber. Afdeel. Handelsmuseum Ver. Koloniaal Inst.* **34,** 3–14(1928).—The rubber made from the latex of *E. dregeana* and other *Euphorbia*

species has very little similarity to real rubber. From a sample of coagulum from the *E. dregeana* Bush rosin and rubber were prepd. The former was very impure, being of a soft and a hard texture and of apparently no value, while the latter was a thin soft mass. The *Hevea* culture need not fear any competition from this source. J. C. JURRJENS

Belt dressing for eliminating static. P. W. EDWARDS AND J. O. REED. *India Rubber World* **80,** 60(1929).—Static electricity can be eliminated from rubber or leather belts by the use of special belt dressings. A good non-static rubber belt dressing contains spar varnish 82, lampblack 18; it is allowed to dry before running the belt. For leather belts the following mixt. is especially good: liquid fish glue 100, glycerol 80, sulfonated castor oil 100, water 170, 2% NH_4OH 20 cc. and lamp black 82 g., in some cases more fish glue and glycerol being advisable. Conditions favoring the production of static electricity and methods of preventing it are described. C. C. DAVIS

The generation of rubber. R. L. DUPONT. *Rev. gén. mat. plastiques* **4,** 621–3, 745–51(1928); **5,** 237, 239(1929).—A review. A. PAPINEAU-COUTURE

Rubber, with special reference to the use of lead compounds. J. R. SHEPPARD. *Trans. Am. Inst. Chem. Eng.* **20,** 187–212(1928).—A review and discussion, with illustrations and tabulated data, dealing with the phys. properties of vulcanized rubber, vulcanizing agents, accelerators and compounding ingredients, with particular reference to Pb compds. C. C. DAVIS

Active fillers for rubber. MARJA SAGAJLO. *Przemysl Chem.* **13,** 154–7(1929).—A review with bibliography. A. C. ZACHLIN

Coagulation phenomena in Hevea latex. VIII. Influence of some heavy metal salts on coagulation and coalescence. OTTO DE VRIES AND N. BEUMÉE-NIEUWLAND. *Arch. Rubbercultuur* **13,** 125–204(1929); (in English 205–18); cf. *C. A.* **23,** 1771.—In studying the effect of $MnSO_4$, $CuSO_4$, $NiSO_4$ and $HgCl_2$ on coalescence and coagulation, the aq. salts were added to undild. latex, to latex dild. to various degrees and to heated dild. latex, with and without the simultaneous addn. of AcOH, the addns. to heated latex being for the purpose of detg. the influence of the salts on the coalescing power of fresh latex and of exts. contg. coalase. The results of the expts. are summarized in the following data, the arithmetical values representing in all cases the concn. of the salt in mg.-mols. per l. in the liquid in question: *Coalescing power* (in B mixt.).—$MnSO_4$, weak, coalescence in 24 hrs. by 35 and in 2 days by 10; $NiSO_4$, no effect; $CuSO_4$, weak, coalescence in 24 hrs. by 64 and a trace of coalescence in several days by 32; $HgCl_2$, distinct, coalescence in 2.5 hrs. by 40–50, in 24 hrs. by 20 and a trace in several days by 2.5. *Coagulating power.*—$MnSO_4$, distinct, coagulation in undild. latex in 1–2 hrs. by 13, flocculation in dild. latex (1:9) by 7 and coagulation in undild. latex (1:9) in a short time by 33; $NiSO_4$, distinct, coagulation in undild. latex in 0.25 hr. by 16, and in dild. latex (1:9) a clot in 0.25 hr. by 8; $CuSO_4$, distinct, in undild. latex a thickening or pasty condition by 10–20, coagulation in 24 hrs. by 30–60, and in dild. latex (1:9) flocculation by 2 and coagulation in a few hrs. by 30; $HgCl_2$, distinct, undild. latex became viscous with 5–10 and coagulated in 24 hrs. with 40, and dild. latex (1:9) flocculated with 1 and coagulated in 24 hrs. with 20. *Effect on heated latex (1:9 B mixt.) without acid.*—$MnSO_4$, flocculation by 3.3, coalescence after 3 days by 33, and after 2 days by 80; $NiSO_4$, flocculation (with a white serum) by 2.4, flocculation (with a clear serum) by 40, with no coalescence; $CuSO_4$, flocculation in 24 hrs. by 8, rapid flocculation, by 64, coalescence after a few days by 46; $HgCl_2$, flocculation in a few hrs. by 0.5, coalescence in 1 day by 10, coalescence in a few hrs. by 40. *Influence on coagulation by AcOH.*—$MnSO_4$, acceleration caused by 3.3 or more in undild. latex, and by 5–6 or more in dild. latex (1:9); $NiSO_4$, acceleration caused by 8–16 in dild. latex and by 2–6 in dild. latex (1:9); $CuSO_4$, flocculation promoted with formation of a paste or porridge-like mass, but coalescence retarded by 0.8–4, and accelerated by 12–40, while in dild. latex (1:9) syneresis proceeded very slowly; $HgCl_2$, flocculation promoted as with $CuSO_4$, coalescence retarded more strongly than with $CuSO_4$ with 0.5–10, while 75 or more accelerated coagulation. *Destruction of coalescing power of exts.*—$MnSO_4$, no effect, $NiSO_4$, distinct, 40–80 diminishing the power greatly and 130–200 nearly destroying it altogether; $CuSO_4$, strong, the power being destroyed by 0.8 or more; $HgCl_2$, strong, 0.5 or more destroying the power. *Spontaneous coagulation by bacterial acid formation.*—$MnSO_4$, no effect; $NiSO_4$, no effect; $CuSO_4$, coagulation of undild. latex inhibited by 4, and of dild. latex (1:1) inhibited by 2; $HgCl_2$, coagulation of undild. latex inhibited by 5 and of dild. latex (1:1) inhibited by 0.75. $CoSO_4$ was not available, but tests of $Co(NO_3)_2$ indicated that it would have much the same properties as $NiSO_4$. The results show that the phenomena are varied and complicated. $MnSO_4$, $NiSO_4$ and $Co(NO_3)_2$ showed in general the normal behavior of bivalent salts except that $NiSO_4$ in high concns. diminishes the

coalescing power and has no coalescing power itself (whereas $MnSO_4$ has a weak coalescing power). $CuSO_4$, however, acts abnormally, particularly in that coagulation by AcOH is greatly retarded at certain concns. of $CuSO_4$, and in that the coalescing power of fresh latex and exts. is diminished or destroyed. $HgCl_2$ is also noteworthy in its power of destroying the coalescing power of fresh latex and exts. contg. coalase. $AgNO_3$ (0.6 and 1.2 mg.-mols. per l.) did not coagulate dild. latex (1:1); in fact, spontaneous coagulation was retarded. Coagulation by AcOH is uninfluenced by 0.6 mg.-mols. and is retarded by 1.2 mg.-mols. It has a weak coalescing effect. C. C. DAVIS

Volume compounding. F. HARRIS COTTON. *India Rubber J.* **77**, 583–4(1929).—A discussion of the principles. C. C. DAVIS

China clay as a reënforcing agent in rubber compounding. T. J. DRAKELEY AND W. F. O. POLLETT. *Trans. Inst. Rubber Industry* **4**, 424–60(1929).—Since clays are cheaper than C blacks and can also be used in light-colored rubber products, an extensive investigation was made of the suitability of china clays as reënforcing agents and the quality obtained in comparison with C blacks under the same conditions. The base mixt. contained: pale crepe 100, ZnO 5, S 4, diphenylguanidine 1, to which were added various proportions of the pigments. The phys. tests of the cured mixts. included the relation between tensile products and times of cure, the influence of temp. on the stress-strain curves, stress-strain curves and their comparative curvatures, resilient energy, the effects of softeners and the relative stiffness of the various samples. The data are given in detail in tables and graphs, and the results may be most readily summarized from the following conclusions: None of the clays retarded the rate of vulcanization, and some had a mild accelerating action. On the other hand, the C blacks had a retarding action. The accelerating action of some clays was probably closely related to their alkali content, for equiv. quantities of Na_2CO_3 had the same effect. Small proportions of stearic acid did not influence the accelerating action of the clays, but did eliminate the retarding action of the C blacks. The extent of these accelerating or retarding effects was proportional to the quantity of pigment. The lower the temp. at which the mixts. were tested, the lower the elongation and the greater the tensile strength. Increasing proportions of clays displaced the stress-strain curve toward the stress axis in a way typical of reënforcing pigments. Up to 18% by vol. (based on the rubber) the clays increased the tensile strength, and the best clays increased the tensile strength more than did equal vols. of the C blacks. Up to 25% by vol., the clays increased the resilient energy, the max. being reached at about 12%. These max. resilient energy values were greater than the corresponding ones with C black, but the clays failed to reënforce at such high loadings as the best C blacks. Small proportions of stearic acid did not influence the % vol. of clay or of C black at which the max. energy values occurred. With clays, stearic acid reduced the tensile strength and resilient energy values, whereas with C blacks it increased it. The slope of the stress-strain curve of the base mixt. was increased at first by clay or C black, but in some cases a max. was reached, beyond which the slope diminished with more pigment. The stress required to obtain a given elongation does not represent the stiffness of a cured mixt., particularly when the effect of increasing proportions of pigments is taken into account. Stiffness is more satisfactorily expressed by the elongation which a given stress produces. The C blacks increased the stiffness more than did the corresponding vols. of clays and, though stearic acid was without effect with small proportions of pigment, at higher proportions it further increased the stiffness. This stiffening action of the clays and C blacks had little relation to their effects on the tensile strengths. Clays did not increase the concavity factor (cf. Wiegand, *C. A.* **19**, 2423, 3386) of the base mixt. so much as did the same vols. of the C blacks. With increase in the % pigment, the effect on the concavity factor gradually diminished, while this factor was not affected by small proportions of stearic acid. C. C. DAVIS

The influence of selenium red on the physical properties of accelerated rubber mixtures. RUDOLF DITMAR. *Chem.-Ztg.* **53**, 239(1929).—A study of the action of Se red (cf. *C. A.* **23**, 1526) on the phys. properties of rubber-S-ZnO-$CaCO_3$-Se red-accelerator mixts. vulcanized with 19 different accelerators showed that it behaves like the com. grade of Se called "Vandex," the reënforcing effect depending upon the accelerator and being inappreciable with some accelerators. C. C. DAVIS

The behavior of the selenium preparation "Vandex" in rubber mixtures. RUDOLF DITMAR AND MANFRED RACHNER. *Gummi-Ztg.* **43**, 1583–4(1929).—Tests of the phys. properties of different cured rubber mixts. contg. Se (in the form of Vandex) show that (1) in a mixt. contg. rubber 100, S 5, $CaCO_3$ 20, Vandex 2, the Vandex stiffened the cured mixt., whereas with much higher proportions this stiffening action was diminished; (2) in a mixt. contg. rubber 100, S 5, ZnO or PbO or MgO 10, $CaCO_3$ 20, Vandex 2, the Vandex had a stiffening effect with ZnO, but had no effect with PbO or MgO;

(3) in a mixt. contg. rubber 100, S 3, PbO 10, $CaCO_3$ 30, accelerator 2, Vandex 2, the Vandex had a stiffening effect with some accelerators, whereas with others it had no effect; and (4) in a mixt. contg. rubber 100, S 3, ZnO 10, $CaCO_3$ 30, accelerator 2, Vandex 2, the Vandex had a high stiffening effect with some accelerators, whereas with other accelerators its effect was negligible. The accelerators with which Vandex showed a stiffening effect in conjunction with PbO were different in some cases from those accelerators with which it showed a stiffening action with ZnO. Therefore the stiffening action of Vandex depends upon the accelerator and other factors, and it must be detd. for the individual case. C. C. DAVIS

The nature of vulcanization. IV. H. P. STEVENS AND W. H. STEVENS. *J. Soc. Chem. Ind.* **48,** 55–9T(1929); cf. *C. A.* **22,** 1703.—A survey of the literature shows that there is still uncertainty concerning the max. proportion of S, which under the most favorable conditions will combine with rubber on vulcanization. Expts. were therefore carried out, under conditions different from those of previous investigators, to det. the *max. limit of combined S.* Prolonged vulcanization was carried out at 100° by the aid of Zn diethyldithiocarbamate (cf. *British Patent* 269,693, *C. A.* **22,** 1498), which minimized the decompn. of the rubber. If the Zn diethyldithiocarbamate remained unaltered during vulcanization, it would be removed on acetone extn., whereas if it were decompd., ZnS would be formed. The technic took care of each possibility, the acetone-extd. rubber having been analyzed directly for combined S, and the vulcanizates also having been extd. with HCl in Et_2O to remove any ZnS. The results were such that, even if all the Zn were converted to ZnS and allowance were made for this in the calcns., the combined S of the hard rubber was considerably in excess of that corresponding to C_5H_8S. Extn. of the hard rubber with HCl-Et_2O mixt. removed part of the combined S; the greater the proportion of the latter the more was removed, but in all cases the proportion remaining was considerably greater than that corresponding to C_5H_8S. This was true whether the rubber was ordinary crepe, sprayed rubber or partially purified rubber, whether vulcanization was carried out in the ordinary way or by the solvent method of Whitby and Jane (cf. *C. A.* **20,** 2763), and regardless of the excess S. With prolonged vulcanization, the proportion of combined S depended chiefly upon the excess of S. The H_2S and other volatile S compds. evolved in appreciable quantities during vulcanization being considered, the results show that part of the combined S is accounted for by substitution of H by S. This substitution product is decompd. by the treatment with HCl-Et_2O mixt., though it is probably impossible to decomp. all of this S-substitution product. Consequently, any combined S in excess of that corresponding to C_5H_8S may be the result of substitution. Degradation products contg. combined S were not formed, the brown substance remaining in the acetone ext. after removal of free S from the latter contg. no S compds. but probably being composed of decompn. products derived from non-rubber components. Even with continued acetone extn. for several months, small quantities of free S were still being removed. C. C. D.

New microscopic methods in connection with the problems of vulcanization. E. A. HAUSER, H. MIEDEL AND M. HÜNEMÖRDER. *Colloid Symposium Monograph* **6,** 207–17(1928).—By means of a tiny vulcanization chamber, which is illustrated, vulcanization of the following mixts. was followed microscopically: (1) 100 rubber, 3 S; (2) same as (1) plus 5 ZnO; (3) same as (2) plus 1 accelerator. With (1), when undercured, S reappears as colloidal globules which grow and form dendrites. ZnO retards this process, dendrites being marked. Accelerators seem to prevent sepn. of the S, except at the surface (blooming), and may thus be recognized. Thiuram disulfide slowly forms needle-shaped deposits, which aggregate into half-moon shaped crystals of unknown compn. While (1) and (2) show marked flow at the beginning of vulcanization, (3) shows only slight flow, which stops abruptly. Ether-sol. α-rubber vulcanizes more slowly and requires a higher temp. than whole rubber, or β-rubber. The view is advanced that vulcanization "depends on minute traces of a substance present in crude rubber, a substance which firmly adheres to the α-fraction, so that it can be removed only after this fraction has been isolated from its original combination in the rubber." JEROME ALEXANDER

The consumption of accelerator during vulcanization. L. v. WISTINGHAUSEN. *Kautschuk* **5,** 57–61, 75–7(1929).—The extent to which accelerators of different types disappear during vulcanization was studied by curing accelerated base rubber mixts. with different proportions of S, with and without ZnO, and by detg. the proportions of accelerator remaining after increasing times of cure. The 2 accelerators chosen were diphenylguanidine (**I**) and mercaptobenzothiazole (**II**). Throughout the expts. they were used in the same proportion by wt. The stress-strain curves of the vulcanizates were also obtained to det. whether there is any relation between the stability or fugitiveness of an accelerator and its activity. In all cases the consumption of **I** and **II**

increased progressively with the duration of cure, approaching a max. in each case. All the results are given in graphical form, and it is this max. which shows most clearly the influence of the type of rubber, the type of accelerator, the % S, the presence or absence of ZnO and the time of vulcanization on the extent of the disappearance of the accelerator. Without ZnO, I disappeared much more rapidly than II, and this was reflected in a greater accelerating power by I, the stress-strain curves showing stiffer, stronger vulcanizates for given cures. With other conditions equal (with or without ZnO, etc.), more I and II disappeared with 1st latex crepe than with sprayed rubber or Peru rubber. This had no relation to the phys. properties of the vulcanizates, for the stress-strain curves bore no relation to the accelerator consumption. The disappearance of I and II was smallest without ZnO; with increasing proportions of ZnO (up to 12 parts per 100 parts of rubber) progressively higher proportions of I disappeared. The stress-strain curves showed that ZnO had an activating effect. Without ZnO, the higher the % S the greater the proportion of I but the less the proportion of II which disappeared. With ZnO, the higher the % S the greater the proportions of both I and II which disappeared. In all cases the rate of vulcanization (judged by the stress-strain curves) increased with the % S. The results indicate that the accelerating power depends in some way upon its reactivity and disappearance in the reaction, rather than upon a catalytic effect. Where no appreciable part of the accelerator disappeared, there was no accelerating effect. The formation of complexes of accelerators and Co salts of unsatd. org. acids makes it probable that complexes of I and II with ZnO are formed during vulcanization. Such complexes would increase the soly. of the accelerator in the rubber, and would also increase the electropositive state of the Zn and thus activate the S (cf. Scholz, *C. A.* **21,** 2399). The increase in consumption of accelerator with increase in the % S indicates, furthermore, that S takes part in this complex formation. It is also possible that a rubber-accelerator compd. is formed. The expts. were not carried far enough to find a relation between the consumption of accelerator and the increase of combined S (cf. Hardman and White, *Gummi-Ztg.* **1927,** 305; cf. *C. A.* **21,** 4098). Twiss has already found (*Gummi-Ztg.* **1928,** 2307; cf. *C. A.* **22,** 2491; **23,** 2070) that a combined S-cure curve gives no indication of the optimum cure, and similarly the present expts. show that there is no apparent relation between the progressively increasing consumption of accelerator and the changes in phys. properties. The consumption of accelerator was measured indirectly by detg. the residual accelerator extractable with hot acetone. *Detn. of I.*—Ext. 20 g. of finely divided rubber for 12 hrs. in a Soxhlet app. with acetone, evap. the ext., dissolve in Et_2O, add 10 cc. of aq. 0.1 *N* HCl, evap. the ether, cool, filter, dissolve the residue in Et_2O, treat as before with HCl; repeat this 3 times; wash the final residue with water; to the combined filtrates (not over 50 cc.) add 50 cc. of 1% aq. picric acid, let stand overnight, filter through a weighed Gooch crucible, wash with 5 cc. of water, and dry at 100°. With overcured vulcanizates the final picrate may have a dark brown color, and probably contains decompn. products. *Detn. of II.*—Ext. 100 g. of finely divided rubber for 12 hrs. in a Soxhlet app. with acetone, evap. the ext., dissolve the residue in 20 cc. of warm C_6H_6, filter, wash with C_6H_6; to the filtrate add an excess of 3% filtered C_6H_6 soln. of Cu oleate until the soln. remains green and let stand overnight; centrifuge, wash the ppt. with C_6H_6 and then with petr. ether, dry at 140° and weigh. The reaction is: $2II + Cu(C_{18}H_{33}O_2)_2 \longrightarrow 2C_{18}H_{34}O_2 + CuC_7H_4NS_2 + C_7H_4NS$, the C_6H_6-sol. Cu salt which is formed being transformed into a C_6H_6-insol. Cu salt and dibenzothiazoledisulfide (like the decompn. of $Cu(CN)_2$ to CuCN and $(CN)_2$). In the Cu ppt. is 0.5 of the II, so that this must be multiplied by the factor 1.4556 to obtain the quantity of II extd. by the acetone. C. C. DAVIS

The oxidation of vulcanized rubber. A. VAN ROSSEM AND P. DEKKER. *Rubber Age* (N. Y.) **25,** 85–8, 143–5(1929).—An English version of *C. A.* **23,** 2598. C. C. D.

Onazote. J. C. G. KUNHARDT. *Bull. Rubber Growers' Assoc.* **11,** 222–8(1929).—"*Onazote*" is a type of vulcanized rubber which has been made to absorb a neutral gas under pressure during vulcanization and is thus expanded into a highly cellular condition. The gas is retained under pressure, and the product may be molded into any desired form, and can be made soft and resilient, or hard. Unlike sponge rubber it is non-absorbent and has certain notable characteristics, *e. g.*, (1) it is the best non-conductor of heat; (2) it is the lightest solid known (3–7 lbs. per cu. ft.); (3) the soft variety is by far the most compressible solid in existence and has a recovery almost the same as that of air; (4) it is an extremely efficient absorber of shock and vibration; (5) it is probably the best non-conductor of sound; and (6) its great expansion during vulcanization allows better molding than ordinary rubber mixts. The unique properties of Onazote make it of great value for a very wide variety of uses, many of those already tried or suggested being mentioned. C. C. DAVIS

Temperature coefficient of vulcanization of a litharge compound. J. R. SHEPPARD. *India Rubber World* **80,** 56–60(1929); cf. *C. A.* **22,** 4272.—Exptl. data on the stresses at intermediate elongations, tensile strength, ultimate elongation, tensile product, energy and free S of a mixt. contg.: rubber 100, S 8, PbO 15, stearic acid 1 and ZnO 44, vulcanized to different degrees, were utilized to construct graphs showing the time of cure as a function of the temp. for const. values of the 6 properties mentioned above. There were no significant differences in the temp. coeffs. for the several properties. The coeffs. of the various properties varied from 12.6 for strength at 300 and 600% elongations to 13.7 for tensile product, with an av. of 13.1, *i. e.*, to halve or to double the time of cure required a change of 13.1° F. This method may be applied to the study of vulcanization in general and to accelerator action in particular, *e. g.*, the more exact evaluation of the suitability of an accelerator for low or high temp. cures, the comparative effects of various methods of curing (air, steam, mold, etc.), the instability of accelerators to avoid scorching, comparisons of different activators with different accelerators, the adsorption of accelerators by reënforcing agents, etc. C. C. D.

Coal-dust firing in the rubber industry. KARL D'HUART. *Kautschuk* **5,** 106–9, 143–4(1929).—A description of recent developments, with diagrams of equipment. C. C. DAVIS

What solvents are most suitable for the rubber industry? F. BOIRY, J. PANEM, WALTER HUTCHINSON, L. SLOÏM, GODEL AND C. SERVILLE. *Rev. gén. caoutchouc* **6,** No. 51, 9–12(1929).—Comments from different points of view, on the characteristics of well-known solvents and their individual advantages and disadvantages. C. C. DAVIS

Zinc oxide for the rubber industry. HARRY E. OUTCAULT. *India Rubber World* **80,** No. 4, 70(1929).—A general review and description. C. C. DAVIS

Isoprene and rubber. XV. H. STAUDINGER. *Kautschuk* **5,** 94–7, 126–9(1929); cf. *C. A.* **23,** 3372.—A detailed review and discussion of recent investigations by different experimentors on the *chem. constitution of rubber, gutta-percha* and *balata.* Numerous references are included. C. C. DAVIS

The dispersion of carbon black in rubber. Comparison of the heats of wetting of raw rubber and different samples of carbon black. L. HOCK. *Kautschuk* **5,** 147 (1929).—Tests of the heats of wetting (cf. Hock and Bostroem, *C. A.* **21,** 1335) of 2 C blacks (Durex I extra and D 7 of Wegelin A.-G., Köln) gave values of 7.12 and 3.89 cals., resp., per g. of C black immediately after mixing. After standing, the heats of wetting increased, indicating that on standing combination between rubber and pigment progressed further. C. C. DAVIS

The dispersion of carbon black in rubber. Microscopic examination of carbon black in rubber mixtures. M. HÜNEMÖRDER. *Kautschuk* **5,** 147–8(1929).—A study of the ease of dispersion and behavior during vulcanization of the 2 blacks examd. by Hock (cf. preceding abstr.) showed that Durex 1 extra is finer and can be dispersed better than the other black. During vulcanization the finer black dispersed still more until plastic flow ceased, whereas the coarser black retained its original state of dispersion. C. C. DAVIS

Dispersion of pigments in rubber. II. ERNST A. GRENQUIST. *Ind. Eng. Chem.* **21,** 665–9(1929); cf. *C. A.* **22,** 4875.—Expts. are described which show the microscopic structure of raw rubber under various conditions, the size and shape of C black particles, the wetting capacity of C black in water and in rubber and the behavior of rubber resins, S, ZnO, C black, stearic acid and accelerators in rubber during heating and during vulcanization. Reënforcement of rubber by a pigment depends upon 3 fundamental factors: (1) the free surface energy of the system, which is governed to a considerable extent by the size, shape and uniformity of the particles and their dispersion; (2) the intensity of wetting of the pigments by the rubber or of the rubber by the pigments, which is governed by the state of dispersion, the nature of the surfaces of rubber and pigment and the surface-active substances adsorbed at the interface; and (3) the strength of the rubber matrix, which is governed by the degree of polymerization, the state of globular structure and the action of dissolved substances and compounding ingredients. C. C. DAVIS

The electrokinetic potential of rubber. B. N. GHOSH AND P. STAMBERGER. *Kautschuk* **5,** 99–100(1929).—A preliminary note. The electrokinetic potential of rubber with water and 7 solns. of different concns. was measured, the electroëndosmotic capillary transference method with a modified form of the app. described by Briggs (cf. *C. A.* **13,** 1784) being used. The rubber capillaries were prepd. from latex and a C_6H_6 soln. of rubber, the same results being obtained in each case. Measurements were made at 200 v. in the usual way. The elektrocinetic potential ζ was calcd. from the formula $\zeta = 4\pi\eta vl/(ERq)$, where η is the viscosity of the liquid, v the quantity of

liquid transferred per sec., E the voltage (200) and l/q the ratio of the length to the cross section of the capillary. The following ζ values were obtained, the data giving the normality of the soln. and the ζ value in v., resp.: water—, −0.038; NaOH 0.005, −0.048; 0.010, −0.048; 0.025, −0.067; 0.50, −0.060; 0.100, −0.072; NH_4OH 0.08, −0.045; 0.32, −0.059; 0.76, −0.066; HCl 0.033, −0.021; 0.05, −0.023; AcOH 0.23, −0.038; 1.0, −0.052; 2.0, −0.059; KCl 0.02, −0.031; 0.04, −0.028; $BaCl_2$ 0.01, −0.019; 0.03, −0.015; $Th(NO_3)_4$ 0.1, 0.015; 0.3, 0.019. To what extent the electrokinetic potentials measured in this way correspond to those of rubber latices, and in what way the potential and stability are influenced by changes in compn. are being investigated. The expts. are also to be continued with other substances.

C. C. DAVIS

Mechanical tests of rubber and probabilities. R. FRIC. *Rev. gén. caoutchouc* **6**, No. 51, 3–8(1929).—See *C. A.* **22**, 4870. C. C. DAVIS

Some observations on rubbers with low nitrogen content. A. D. CUMMINGS AND L. B. SEBRELL. *Ind. Eng. Chem.* **21**, 553–7(1929).—Rubber cannot be prepd. free of N by the method of Pummerer and Pahl (cf. *C. A.* **22**, 885) even by continuing the treatment with NaOH for twice as long as recommended by P. and P. The residual 0.004–0.009% N is not protein N, since it can be removed by extn. with acetone to a point where it is so low that it cannot be detd. precisely by the colorimetric method with Nessler soln. Comparison of the results of vulcanizing protein-free rubber with the corresponding results with untreated rubber, and with the results of previous researches, shows that the rate of vulcanization is const. for different conditions of coagulation. Furthermore, the quality of vulcanizates low in N is very good compared with the quality of the corresponding controls and earlier expts. described by Dinsmore (cf. *C A.* **21**, 194). The variation in the rate of vulcanization and in the quality noted by D. was, therefore, a result solely of the condition of the rubber protein resulting from the p_H value during coagulation. After extn. with acetone, protein-free rubber is practically free of N, and it vulcanizes slowly, giving vulcanizates of poorer quality than the corresponding ones obtained from the unextd. protein-free rubber This effect may, however, not depend wholly upon the absence of N compds. Protein-free rubber can be compounded and cured so that vulcanizates of good quality are obtained, so the protein is not an essential factor governing the phys. properties of vulcanized rubber. The condition of the protein does, however, influence the rate of vulcanization, and consequently affects indirectly the quality of the vulcanized rubber. C. C. DAVIS

A new flexing machine for rubber. PHILIP M. TORRANCE AND LESTER C. PETERSON. *India Rubber World* **80**, No. 4, 62(1929).—The new app., which is described and illustrated, is designed to imitate the cracking of tire treads in service. Results show a qual. agreement with road tests. Based on these lab. tests, it was found that some antioxidants reduce tread cracking, whereas others have no such beneficial influence. The conditions during processing and the modulus also influence the tendency to crack. "Cold checks" and grain cause premature cracking, phenomena which are probably related to the premature cracking at the junction of the tread and sidewall of a tire. The app. should be particularly useful in studying temp. effects.

C. C. DAVIS

Sipalin, a new light colored plasticizing agent for rubber. RUDOLF DITMAR. *Gummi-Ztg.* **43**, 1932–3(1929).—Plasticizing agents marketed under the name *"Sipalin"* (Deutsche Hydrierwerke A.-G., Berlin-Charlottenburg) are esters of adipic acid, *e. g.*, *Sipalin AOM* is the methylcyclohexyl ester of adipic acid and *Sipalin MOM* is the methylcyclohexyl ester of methyladipic acid. They are very effective softeners in that they shorten the time of mixing and allow the use of higher proportions of such pigments and fillers as C black without detriment to the quality. C. C. DAVIS

Fossil rubber. E. KINDSCHER. *Kautschuk* **5**, 98–9(1929).—The geological discovery of vulcanized rubber in brown coal deposits (cf. K., *C. A.* **18**, 2862; Gothan, *C. A.* **19**, 1240; **22**, 933) is of great interest from a practical point of view, for it shows that when rubber is completely protected from oxygen it remains in good condition for many thousands of years. C. C. DAVIS

Physical characteristics of sponge rubber. H. F. CHURCH. *Trans. Inst. Rubber Ind.* **4**, 533–42(1929).—Data on the phys. properties of sponge rubber are very few. In the present paper an attempt was made to develop a test which would allow accurate measurements and at the same time give a reliable judgment of the quality. Tensile strength tests cannot be made directly and they do not represent conditions prevailing in use. Methods were developed for detg. the *"cellularity," compressibility* and *permanent set.* Tests on sponges of different types showed that, in contrast to other types of rubber products, the phys. properties of sponge rubber are governed more by the form

of the cell structure than by the phys. properties of the rubber itself. Consequently, the quality of sponge depends relatively little on the compn. of the vulcanizate or on its degree of cure. However, other factors which do depend upon these properties, *e. g.*, the aging, are of importance. Photomicrographs of different forms of sponging are shown. C. C. DAVIS

Aging tests for sponge rubber. HENRY P. STEVENS. *Trans. Inst. Rubber Ind.* **4**, 486–92(1929).—When rubber sponge is compressed laterally between metal plates and heated at 70° for 2–3 days, the rubber does not recover when the pressure is released, but retains the forms of a flat sheet from which test pieces can be cut and tensile tests obtained. Twelve different types of sponge were aged in this way for 1 month and the progressive changes in tensile properties detd. The same samples were aged for 1 week without compression and consequent protection, and the changes in org. acetone ext. detd. The quant. tests revealed wide differences in properties after the artificial aging, not only among different makes but among different samples from the same source. The tests conformed to the results obtained by general examn. and hand tests before and after the artificial aging. C. C. DAVIS

The double refraction of stretched rubber. W. C. VAN GEEL AND J. G. EYMERS. *Z. phys. Chem.*, Abt. B, **3**, 240–6(1929).—Though the double refraction of rubber has already been measured (cf. *Ann. Physik* **43**, 808(1891); Rossi, *Rend. accad. sci. Napoli* [3], **16**, 125, 142(1910); *Nuovo cimento* [5], **20**, 226, 268(1910); [6], **2**, 151(1911)) no relation between elongation and double refraction has been described. Accordingly, expts. were carried out to ascertain the existence of such a relation. Films of raw rubber, prepd. by drying fresh latex, were examd. with a Babinet compensator. Rubber, which had been plasticized by milling, was also examd. in a similar way. With elastic rubber under a const. stress, the elongation reached a const. value in a very short time. When equil. was thus reached, the double refraction was measured. New samples were used for each increased stress, for with the same sample a repeated stress of const. magnitude gave increasing double refractions. The curves showing double refraction as a function of stress were very similar to those showing the double refraction of liquid crystals as a function of field strength in a magnetic field (cf. Ornstein, *C. A.* **18**, 2827). An anisotropic alignment of mols. like that suggested by Ornstein probably exists in the stretched rubber. On this assumption, analogous curves were constructed, with the *b* value of the Ornstein formula proportional to the elongation. Comparison of these curves with exptl. curves showed agreement up to a certain stress. Above this limiting stress, the double refraction increased progressively with increase in stress in a strictly linear relation. This linear relation began in all cases at just the same stress (6 kg. per sq. cm.). The elongation being plotted as a function of stress, the curve showed that at this same stress, which corresponded to 70% elongation, the relation between elongation and stress became strictly linear. This crit. value of 70% elongation is the point at which an x-ray fiber diagram was first obtained (cf. Katz, *Naturwissenschaften* **1925**, 110), and so this point is a characteristic of raw rubber. It probably depends, however, upon the compn. of the rubber and upon the temp. With raw rubber which had been plasticized, there was no equil., a const. stress causing elongation which increased progressively. Double refraction was a linear function of the stress, as with certain liquids. When the plasticized rubber was held at a const. elongation, the double refraction diminished with time, rapidly at first, but more and more slowly, leaving a residual pos. double refraction and also a residual stress. This residual double refraction and residual stress were almost wholly independent of the initial elongation. C. C. DAVIS

The value of reclaimed rubber in tread stock. C. W. SANDERSON. *India Rubber World* **80**, No. 4, 53–6(1929).—A typical high-grade tread stock contg. no reclaim and a stock contg. a high proportion of whole tire alkali reclaim were blended in different proportions (0, 25, 50, 75, 100%); the resulting vulcanizates were tested for their relative resistances to abrasion and for other phys. properties, including resistance to tear, fatigue effects, tensile strength and elongation. The results on the different vulcanizates are compared on an abs. basis (cf. Vogt, *C. A.* **22**, 1058) and on a basis of the relative cost per unit of abrasion. The value of reclaim varied from 25 to 42% of the value of new rubber, the highest value being obtained with the stock contg. no new rubber. With rubber at $.20 per lb., the relative cost of the reclaim per unit of abrasion was above that of rubber in all the stocks, while with rubber at $.40 per lb., the relative cost of the reclaim was less than that of rubber when there was more reclaim than rubber present. Road tests agreed well with the lab. tests. Tensile strength, lamination tear and abrasion with 30% slip gave the best indication of road wear. C. C. DAVIS

Chemical reactions in rubber compounds. I. Reactions between pine tar and

litharge. W. H. Reece. *Trans. Inst. Rubber Ind.* **4**, 526–32(1929).—The expts. are the beginning of an investigation to ascertain what reactions, other than those involving rubber, S and accelerators, take place during vulcanization, knowledge of which is very scant. A com. pine tar with d. 1.07, neutral oils 50.9%, water 1.4%, carbonaceous substances 0.8%, acids (by difference) 46.9% were used. When PbO and anhyd. pine tar were refluxed in C_6H_6 for 24 hrs., a reaction ensued with evolution of water (2.45 g. per 100 g. pine tar) and formation of Pb soaps (corresponding to 30.37 g. PbO per 100 g. pine tar). Similar rubber-pine tar (100:15) mixts. prepd. in the same way with and without PbO were let stand 24 hrs. and their plasticities (extrusion at 85°) detd. The values were 11 and 2.3 sec., resp., showing the pronounced hardening resulting from the reaction of PbO and pine tar. When the 2 mixts. were heated at 70°, that with PbO remained stiff, whereas the mixt. without PbO showed plastic flow. The acetone exts. were 9.11 and 15.81%, resp., from which calcns. show that 43.3% of the pine tar combined with PbO (any reaction between PbO and rubber resins being disregarded). By a special exptl. technic, it was found that when a mixt. of rubber 200, S 6, PbO 30, pine tar 30 was vulcanized, 1.31 parts of water was evolved, compared with 1.17 in the absence of rubber (*loc. cit.*), the excess probably arising from a reaction between PbO and rubber resins. The results in general show that PbO and pine tar react in a rubber mixt. in essentially the same way that they do in the absence of rubber. The values conform with the assumption that the pine-tar acids react with PbO to form soaps.

C. C. Davis

The distribution of ingredients in rubber mixings. H. Page. *Trans. Inst. Rubber Ind.* **4**, 521–5(1929).—The unforeseen results obtained by Reiner (cf. *C. A.* **22**, 2290, 2855) on the homogeneity of factory rubber mixings induced P. to make similar analyses. The results disprove the general conclusions of R. Detns. of the free S and the ash of 7 different types of rubber mixings before and after calendering showed variations which were all well within a fraction of 1%, and which proved, therefore, that with ordinary care in factory mixing, no such variations as reported by R. are at all necessary.

C. C. Davis

Studies in the oxidation of rubber mixings. W. Cecil Davey. *Trans. Inst. Rubber Ind.* **4**, 493–8(1929).—Vulcanized rubber mixts., unaccelerated and accelerated, were cured to different degrees, were then aged in a Geer oven at 70° and the increase in wt. and changes in acetone ext. detd. as deterioration progressed to an advanced stage. In some cases before aging, the vulcanizates were extd. with acetone, in other cases with acetone and then with $CHCl_3$. In still other cases the vulcanizates were given alternate periods of aging and extns. with acetone. *Unextd. vulcanizates.*—The higher the % combined S, the more rapid was the increase in wt. after a given period of aging. During the early stages of deterioration the higher the combined S, the higher the org. acetone ext., whereas in more advanced stages of deterioration the samples with the lowest combined S had the highest org. acetone exts. The formation of acetone-sol. substances was very slow at first; it then became rapid and finally became slow again. *Acetone-extd. vulcanizates.*—Oxidation was rapid, while the acetone-sol. substances increased to a max. proportion and then diminished to a value which remained const. over a long period of subsequent aging. In the early stages, the vulcanizates with the highest combined S showed the highest proportion of acetone-sol. substances, but on further aging these with the lowest combined S eventually yielded the highest acetone ext., so that the higher the vulcanization coeff., the lower the ultimate proportion of acetone-sol. substances. For a given increase in wt., the vulcanizates with the highest combined S gave the smallest acetone ext. *Acetone and $CHCl_3$-extd. vulcanizates.*—Oxidation was still more rapid, and the increases in wt. and in acetone-sol. substances were higher throughout than those of the corresponding vulcanizates extd. with acetone alone. *Repeated aging and extn.*—A vulcanizate alternately aged and extd. with acetone and $CHCl_3$ gave a final insol. residue contg. more O (25.41%) than the same sample alternately aged and extd. with acetone alone (residue contg. 19.15% O). In the early stages of oxidation, the vulcanizate with highest combined S yielded the highest acetone ext., but in the more advanced stages of oxidation, the converse was true. *Aging of the acetone ext.*—On heating at 70°, the acetone exts. gained wt. and became insol. The longer the vulcanizates had been aged before extn. with acetone, the smaller were the subsequent gains in wt. of the exts. *Aging of the $CHCl_3$ ext.*—On heating at 70°, the $CHCl_3$ exts. gained wt. and became insol. in ordinary org. solvents. A vulcanizate accelerated with diphenylguanidine oxidized much more slowly than the corresponding rubber-S mixt., but gained more ultimate wt. and had a higher ultimate acetone ext. The results in general show that there are 3 stages of oxidation: (1) a slight oxidation, with formation of acetone-sol. substances; (2) an intermediate stage, characterized by a rapid gain in wt. and relatively slow formation of acetone-sol.

substances; and (3) a period characterized by an increased rate of formation of acetone-sol. substances, but a const. rate of absorption of O. The change of acetone-sol. to acetone-insol. substances is probably reversible. The 3rd stage is not reached in ordinary practice, while the 2nd stage is the most important, for then the resinous components polymerize and become insol., with resultant brittleness. C. C. D.

Rubber solutions. CACHTEM. *Gummi-Ztg.* **43,** 2099–102(1929).—A review and description, dealing with the prepn., phys. properties and uses of rubber solns. C. C. DAVIS

Is latex a solution of rubber? FINI G. A. ENNA. *Gummi-Ztg.* **43,** 2043–4(1929).—A discussion of the colloid chemistry of latex. C. C. DAVIS

Concerning antioxidants. T. L. GARNER. *India Rubber J.* **75,** 623–4, 634(1929); cf. *C. A.* **23,** 1772.—For ascertaining the general characteristics of an unfamiliar antioxidant, the following mixt. is recommended: pale crepe 100, S 3.5, diphenylguanidine 1, ZnO 3, antioxidant 0.5–1. The vulcanizates should then be tested in a manner which simulates service conditions in the closest practical way. This latter manner of procedure is very important, for there may be little or no relation between the relative merits of 2 antioxidants in preventing oxidation in darkness, cracking from repeated stresses, changes due to sunlight, resistance due to heating or abnormal deterioration caused by overcuring. Tendencies to stain or discolor may also be determinant factors. Tests by G. show that, contrary to general belief, antioxidants have a protective action on gutta-percha and balata. C. C. DAVIS

The automatic control of vulcanization. MATHIAS MOHR. *Kautschuk* **5,** 114–6 (1929).—An illustrated description of app. for temp. control. C. C. DAVIS

An attempt at a rational classification of the principal accelerators of vulcanization. G. MARTIN AND R. THIOLLET. *Caoutchouc & gutta-percha* **26,** 14,494–7; *Rubber Age* (N. Y.) **25,** 201–2(1929).—The object of the study was a classification based not only on activity, but also on other important characteristics of accelerators (cf. Dinsmore and Vogt, *C. A.* **22,** 4273, 4876), *viz.* (1) the time required for the *"fixation"* of rubber mixts. at different temps.; (2) the time required at different temps. to effect a cure with the max. mech. properties; (3) the aging; and (4) the plasticizing power of the accelerators and the influence of different charges on their action. The present paper deals with (1) and (2). The following base mixt. was used: pale crepe 100, S —, accelerator —, ZnO 5, palm oil 1, stearic acid 0.5. To define the *point of fixation,* a mixt. was fixed when (1) without being cured it could be removed from an Al mold without sticking and without distortion; (2) cut surfaces could be reunited; and (3) just before the crit. point the mixt. softened when carried quickly to higher temp., and just beyond the crit. point the mixt. acquired more nerve when its temp. was raised. The point of fixation thus indicates the tendency to "scorch." By plotting temps. as ordinate and times of fixation as abscissa, a series of curves showing the characteristics of each accelerator according to the rate of fixation of mixts. contg. the accelerators was obtained. The accelerators which were tested fell into 6 general groups, typified by (1) Zn isopropylxanthate, (2) Zn methylphenyldithiocarbamate (I), (3) thiocarbanilide (II) and ethylidene-aniline (III), (4) mercaptobenzothiazole (IV) and tetramethylthiuramdisulfide (V), (5) *p*-nitrosodimethylaniline and disubstituted guanidines, and (6) triphenylguanidine (VI), anhydroformaldehydeaniline (VII) and anhydroformaldehyde-*p*-toluidine. Those in (1) caused rapid fixation even at low temps.; those in (2) caused slower fixation so that they can be used with caution in milling operations; those in (3), (4) and (5) caused progressively slower fixations and are still safer; and those in (6) caused fixation only at relatively high temps. V is peculiar, however, in that, when once begun, fixation is extremely rapid, an almost "explosive" vulcanization taking place, with resulting danger of scorching. This classification according to the rapidity of fixation or "precocity of action" serves to distinguish accelerators, *e. g.,* II and VI, or III and diphenylguanidine (VIII), which are ordinarily regarded as similar. Different effects were obtained with combinations of accelerators, mixts. in some cases being more precocious than their components. Thus with 3% S and 0.7% VIII the mixt. was not fixed at 105°, whereas with 2.5% S, 0.4% VIII and 0.3% IV the mixt. was fixed still more rapidly at 105°. Therefore, mixts. of 2 accelerators may be more precocious than either of the components. On the other hand, it is possible to retard the precocity of action of rapid accelerators by the simultaneous use of another. Thus with 1.8% S and 0.7% I, the mixt. was fixed at 100° in 10 min., whereas if 1% VII is added, fixation at 100° occurred only after 30 min. The addn. of accessory ingredients changes these quant. relations, but the results show that it is possible to det. the most suitable degree of acceleration for a rubber mixt. for any particular operating condition. C. C. DAVIS

Tetramethylthiurammonosulfide and tetramethylthiuramdisulfide. HENRI LEDUC,

Rev. gén. caoutchouc **6**, No. 51, 20(1929).—Certain important advantages of tetramethylthiurammonosulfide (I) over tetramethylthiuramdisulfide (II) are cited, including the fact that I is far less active than II below temps. around 115° but just as active above this range, which allows far greater ease of handling uncured rubber mixts. contg. I and allows the prepn. and storage of master batches of I. Contrary to Esch (cf. *C. A.* **23**, 1526, 2323) the activity of I is not impaired by the absence of ZnO.
C. C. DAVIS

Professional saturnism in the rubber industry. F. HEIM DE BALSAC, E. AGASSE-LAFONT AND A. FEIL. *Chimie & industrie* **Special No.**, 739(Feb., 1929).—Investigations carried out in 2 plants showed that danger of saturnism exists in the rubber industry, but that it can be prevented by the usual prophylactic measures. A. P.-C.

Plasticity determinations in crude rubber. VII. Relation between structure and plasticity of rubber prepared in different ways. O. DE VRIES AND N. BEUMÉE-NIEUWLAND. *Arch. Rubbercultuur* **13**, 283–353(1929). (In shorter form in English 354–70.)—Numerous papers in recent years on the relation between the structure of raw rubber and its plasticity have contained interesting hypotheses dealing with the structure of the globules, but have not been supported by exptl. data. On the other hand the investigations of de V. and his collaborators have dealt with the influence of the non-rubber substances and with different methods of coagulation and prepn. These latter investigations have been recently reviewed (cf. *C. A.* **22**, 2077; *India Rubber J.* **75**, 511(1928)), while the present paper is also a crit. review and discussion in amplified form, with tables of quant. data, and with numerous references. This long discussion leads to certain general conclusions. The sol. serum substances have a marked effect on plasticity, rubber with a high content of serum substances becoming harder during storage, whereas rubber with a low content sometimes becomes softer on storage, and when creped is softer even when fresh. The substances which are pptd. from the serum during coagulation (the network of proteins) have little influence on plasticity. Centrifuging and washing the cream gives a plastic rubber which has no tendency to become tacky or to deteriorate on storage, so that this seems one of the few practical ways of obtaining a *more plastic raw rubber*. Swelling with org. solvents, such as C_6H_6 and PhMe, which causes fusion of the rubber globules and union into large units, has an unexpectedly little influence on plasticity, not only when latex is treated with the solvent but also when rubber is dissolved in the solvent and recovered by evapn. This phenomenon is worthy of further study because of its importance in explaining the relation between the structure of rubber and its plasticity. C. C. DAVIS

Importance of temperature and humidity control in rubber testing. II. Resistance to abrasion. W. A. GIBBONS, *et al.* *Ind. Eng. Chem., Anal. Ed.*, **1**, 174–80(1929); cf. Partenheimer, *C. A.* **22**, 511; **23**, 1306.—The earlier investigation was continued with a study of the influence of the temp. and of the relative humidity between mixing and curing on the resistance to abrasion. Four different types of mixts. were tested on two different abrasion machines. The results, which are recorded in tabular and graphical form, and are discussed in detail, admit of certain general conclusions. In detg. resistance to abrasion, the temp. should be controlled within 1° to avoid significant errors from this cause. The relative humidity at which either an uncured or cured mixt. is maintained need not be considered in comparative tests, though when the relative humidity varies over an abnormally great range, greater precision may be attained by conditioning uncured and cured mixts. The temp. at which vulcanizates are ordinarily stored has little effect on their resistance to abrasion. C. C. DAVIS

The influence of the temperature on the strength of fabrics. L. STOLL. *Gummi-Ztg.* **43**, 2218–21(1929).—The results are of importance in *rubber manuf.* because of the heating which fabrics undergo during vulcanization. Samples of a fabric cord were heated at 60°, 80°, 100°, 110°, 140°, 150°, 170°, 200° and 220° for 0.25, 2, 4, 6, 8 and 15 hrs. and the elongation and breaking strength before and after the heating detd. The exptl. results, which are recorded in tables and graphs, admit of certain general conclusions. The higher the temp. and the longer the time of heating the greater is the loss in breaking strength and in elongation. Even after 15 min. of heating, there was a considerable loss of strength, *viz.*, around 4% at 100°, 12% at 150° and 20% at 200°. Up to 110° the loss in elongation and strength may be considered relatively small, while at 140–150° the loss of strength becomes considerable, *e. g.*, around 15% after 2 hrs. C. C. DAVIS

The action of sulfammonium on rubber. R. FRIC. *Chimie & industrie* **Special No.**, 538–9(Feb., 1929).—NH_3 was condensed on S at —80°, a strip of rubber was introduced into the tube, which was then sealed; after 48 hrs. the tip of the tube was broken and during the rapid evapn. of NH_3 the rubber gradually swelled till it practically filled the tube, its surface became coated with pulverulent S, and as the NH_3 escaped by

diffusion it gradually regained approx. its original size, though still retaining a notable deformation. The feel, detn. of combined S, swelling in benzine and mech. strength tests indicated it had undergone at least a slight partial vulcanization, which F. attributes to the action of the nascent S liberated in the decompn. of sulfammonium.

A. PAPINEAU-COUTURE

The influence of sunlight on the color of rubber mixtures. H. RIMPEL AND P. HERRMANN. *Gummi-Ztg.* **43,** 2270(1929).—The exptl. facts described by Defries and Naunton (*C. A.* **23,** 2068) were also discovered by R. and H. and are inc rp rated in a patent, in which they are utilized for the production of pictures or designs on rubber goods (cf. German Patent 448,972). Evidence is given to prove that D. and N. are incorrect in believing that the initial effect of the irradiation is a surface vulcanization and that the discoloration is a result of over-vulcanization on the surface of the vulcanizate. Designs are formed on rubber not only by heating or by vulcanization after exposure, but also by treatment with strong reducing agents, as with light-sensitive AgBr-gelatin. If the reducing agent is mixed into the rubber, it is possible to form designs or pictures directly by exposure to light. When 4 mixts., each contg. rubber, lithopone and ZnO, and the 1st also S, the 2nd accelerator, the 3rd S and accelerator, and the 4th no addn., were exposed to sunlight for 3 hrs. and were then heated at 143° for 30 min., the 1st and 4th mixts. remained unchanged, whereas the 2nd and 3rd mixts. became discolored to an equal extent. This indicates that such discoloration depends only upon the accelerator and that it has no direct relation to the state of cure. The accelerator thus behaves like the reducing agents described in the patent of R. and H. (*loc. cit.*), and the phenomenon is similar to that of a AgBr photographic plate.

C. C. DAVIS

Colloidchemical changes in rubber and fatty oils. LASZLO AUER. *Trans. Inst. Rubber Ind.* **4,** 499–520(1929).—A crit. review and discussion of present knowledge, with certain new points of view and new data. From a colloidal point of view, raw rubber may be regarded as a jelly, β-rubber being the gel skeleton and α-rubber the dispersion medium. β-Rubber therefore corresponds to metastyrene and α-rubber to liquid styrene. β-Rubber is probably only a more concd. soln. of the disperse phase itself, whereas α-rubber is more concd. with respect to the dispersion medium of the jelly than is β-rubber, but it is not the dispersion medium itself. In expts. by Pummerer (cf. *C. A.* **22,** 885, 4873) a better agent than Et_2O could not be found for their sepn., and so in the expts. of P. probably the only result was the concn. of one of the two phases of the jelly, the pure phase not being isolated at all. X-ray investigations agree with this (cf. Bary and Hauser, *C. A.* **22,** 4005), diagrams of frozen rubber indicating an increase in β-rubber at the expense of α-rubber. That coagulating agents aggregate rubber and solvents disaggregate it is supported by unpublished expts. of Stamberger, who has found that when org. solvents, *e. g.*, CCl_4 or Et_2O, are added to latex, and the water and solvent are then evapd., the film has not its usual solid character but is a very sticky paste. After a few days this stickiness disappears and the film acquires a normal condition. In this case the disaggregating agent probably retards the aggregation by air. A discussion of the drying of fatty oils and the extensive expts. of A. in this field, which led to the gas coagulation theory of drying (cf. *C. A.* **20,** 3827; **21,** 3475, 3789; **22,** 1695; **23,** 2089) led to the conclusion that the coagulation of latex on exposure to air is caused by the coagulating action of O. In prepg. Para rubber, the gases in the smoke cause coagulation and aggregation, and the smoking process for smoked sheets involves a similar action. Rubber jelly has a smaller adsorptive power toward coagulating gases than the jelly of fatty oil films, hence the better aging of rubber. Rubber may be considered as a jelly composed of 2 phys. different phases of the hydrocarbon, the structure thus being like a gelatin hydrogel, plasticizing of rubber being like the mech. working of other jellies. Ions act as coagulants, and in gas coagulation gaseous ions are the active agent. Ultraviolet rays ionize gases and their action on fatty oils may be due to the ionization of dissolved O. Just below the b. p. of an oil the gas is evolved and the friction may change the gas electrically and so alter the colloidal structure of the system. In expts. on the *bodying of oils in vacuo*, large proportions (12–61% of the total acids obtained by hydrolysis) of acids insol. in petr. ether were formed, whereas before heating the proportion was small. This shows that the change from sol. to insol. acids is not a result of oxidation. The *mastication of rubber* may be explained by the 2-phase theory, but possibly gas peptization assists the mech. working, *i. e.*, the latter may cause gas peptization. The jelly contains adsorbed O which may be ionized by the friction. This agrees well with facts observed by Fry and Porritt (*C. A.* **22,** 4870). Gases other than O can also cause peptization, but longer times are required (cf. Pummerer and Pahl, *C. A.* **22,** 885). When rubber mixts. contg. considerable C black are stored

before curing, the plasticity disappears and the mixt. acquires some of the properties of vulcanized rubber. When sep. layers are plied and cured under pressure the layers do not unite because a thin film on each surface is formed as a result of coagulation by adsorbed gases. The impossibility of extg. all S from vulcanized rubber does not necessarily signify a chem. combination. Removal of an adsorbed substance can be accomplished by (1) a substance which is more readily adsorbed by the adsorbing product than is the previously adsorbed substance (S), or (2) a solvent with a higher affinity for the adsorbed substance (S) than has the isocolloidal rubber or fatty oil. In each the agent must come into intimate contact with the adsorbed substance (S). S is enclosed in an aggregated system and the agent must also be a disaggregating agent. Therefore so-called combined S has not been removed except by such agents as $PhNH_2$ + K and by concd. HCl. Moreover, the adsorptive power of some systems is stoichiometrical, so even if an apparent limiting value of "combined" S has been found by most investigators (cf., however, Stevens, *C. A.* **23,** 3596) it may signify merely a satn. of the adsorptive power. Bacon (cf. *C. A.* **22,** 3804) did not necessarily wet the aggregated rubber with his desulfurizing agents. His fractional peptization expts. are difficult to reconcile with the chem. combination theory, and finally his limit of 0.5% combined S represents the threshold value of S adsorbed during the aggregation of rubber contg. an accelerator. A discussion of the two most satisfactory theories of *vulcanization, viz.*, the S coagulation or aggregation theory and the chem. theory (cf. Stevens, *C. A.* **22,** 1703), points to the former as the more probable, with the accelerator playing the part of a sensitizer of coagulation by S, like the sensitizing action of Co linoleate on HCO_2H in the coagulation of fatty oils (cf. A., *C. A.* **21,** 3789). When rubber is heated for a long time *in vacuo* at 250° it fuses to a viscous liquid, which on cooling does not revert to the original condition. The loss of wt. is only about 1% and no chem. decompn. can be detected. This *disaggregated rubber* resembles viscous heat-bodied stand oils, and can be vulcanized to products similar to the latter. Both this aggregated rubber and vulcanized rubber have corresponding types in fatty oil derivs., and the new solidified oil derivs. contg. electrolytes are the initial attempts to obtain *oil products resembling raw rubber.* In vulcanized form, these solidified oils have properties more nearly like rubber than any previously known oil product. Data show the *tensile strengths and elongations of rubber mixts. contg. vulcanized solidified oils* compared with those of the corresponding mixts. contg. ordinary vulcanized oils (factice). *Vulcanized solidified oils* are excellent ingredients; *e. g.*, when 50 parts are added to 100 parts of rubber, the vulcanizates have tensile strengths as high as, or even higher than, the corresponding vulcanizates contg. no such addn. of oil product, in contrast to ordinary vulcanized oils, which greatly lower the tensile strength of vulcanized rubber. The jelly system of solidified fatty oils can be further aggregated. S aggregates solidified fatty oils as it does rubber and raw oils. The solidified oils require less S than raw oils and in *varnishes* they require less O than raw oils. Accordingly varnishes contg. solidified oils dry more rapidly than the corresponding varnishes contg. raw oils, with correspondingly smaller adsorption of O. The latter fact explains the better aging of solidified oils. When electrolytes are milled into raw rubber and the mixts. are then heated, products resembling the thermoplastic rubber products of Fisher (cf. *C. A.* **22,** 887) are obtained. The latter were regarded as simply isomerization products, and the fact was overlooked that they were polydisperse systems in which the presence of the reagents or their decompn. reagents are necessary to the resulting properties. The excess reagent used by F. can be washed out, leaving the essential adsorbed part. The case is therefore analogous to the vulcanization of rubber with S partly extractable by acetone. The reactions of F. are also analogous to the action of electrolytes on fatty oils, in each case the dispersed phase being increased. The white powders pptd. by acetone from solns. of thermoplastic rubber products are probably the gel skeletons of the original jellies. Both with thermoplastic rubber products and with solidified oils, the aggregating action of the reagents is more limited than that of S or of gases, and both products may be further aggregated by S or by gases. The increased soly. of thermoplastic rubber products in org. solvents corresponds to the property of solidified oils of being readily emulsified in water. This probably does not depend upon a lower degree of aggregation of the jelly, but because the adsorbed reagent has a higher affinity for the solvent then for the jelly in which it is adsorbed. The solvents may, however, be disaggregating agents.

C. C. DAVIS

Preparation and properties of aqueous rubber dispersions. H. L. TRUMBULL. *Colloid Symposium Monograph* **6,** 215–24(1928).—Aq. dispersions of rubber can be obtained by masticating rubber or reclaim with protective colloids like glue, Na resinate, gum arabic, gluten, Na alginate blood albumin and casein (see U. S. P. 1,498,387).

Such dispersions differ from latex in being free from pear-shaped particles, giving a dried film different in texture, tackiness and strength and being under control of the maker. JEROME ALEXANDER

The reduction of rubber stress-strain determination. W. B. WIEGAND AND H A. BRAENDLE. *Ind. Eng. Chem., Anal. Ed.* **1,** 113–7(1929).—The aim of the work was to find a means of eliminating the personal equation in interpreting stress-strain data. Reduction of 95 tests of an inner tube by statistical methods showed that the stress-strain data did not obey strictly the law of accidental error, the skew being neg. for the values at rupture and pos. at intermediate points. The true values are not therefore the arithmetic means but the modes, which in every case differed from the arithmetic means to an extent greatly exceeding the probable error of such means. By using these true values and dividing the 95 tests into groups of 5, these groups were weighted by 4 empirical methods and the results compared with the modal values. The method of choosing the highest 3 elongations out of 5, with the corresponding tensile strengths, approached most closely the modal values. This method is accordingly suggested as a starting point for a *standardized method of interpreting tests of rubber.* The work is in part a confirmation of expts. on the same subject by Fric (cf. *C. A.* **23,** 4098). C. C. DAVIS

The use of a group of performance tests for evaluating rubber compounds that must withstand repeated compression. HARLAN A. DEPEW AND E. G. SNYDER. *Proc. Am. Soc. Testing Materials* **1929** (preprint) No. 87, 11 pp.—Specifically the present paper gives data on the comparative resistance to abrasion and to pounding of 2 solid tires cured with different proportions of S. The underlying object is, however, to show that by a properly chosen set of lab. tests it is possible to judge the performance of rubber products in actual service. It may be necessary to include with the standard tests an addnl. test which is specially adapted to the particular product which is being developed. The solid tires, which serve as an example, were tested for tensile strength and ultimate elongation, for their hardness and for their resistance to tear, to abrasion and to pounding at different cures. They were also aged in a Geer oven to correlate the phys. properties mentioned above with the uniformity of cure and state of cure at different points in the tires. In the pounding test which is described and illustrated, the samples are subjected to very rapid impacts of high force, and the increases in temp. ascertained. The comparative tests of the 2 tires indicate that a low proportion of S minimizes variability of cure, that the proportion of S does not affect the uniformity of cure throughout the tire when sufficiently long cures are used, and that a high S content tends to low temps. in the tire in service. C. C. DAVIS

Rubber equipment for the chemical industry. ANON. *Ind. Chemist* **5,** 229–36 (1929).—An illustrated description of mfg. operations at the plant of Macinlop, Ltd. (Manchester, England), including rubber-lined tanks, rubber-covered rolls for the paper, bleaching and dye industries, rubber hose, acid valves, acid-proof hose, rubber-lined pumps, fans and ball mills and conveyor belting, with the lab. control of the various processes. C. C. DAVIS

Instrument for reading the hardness or plasticity of rubber optically. R. FRIC. *Chimie & Industrie* **Special No.,** 536–7(Feb., 1929).—The hardness of vulcanized rubber is detd. by placing on the rubber a ball of given diameter, attached to a vertical rod, which in turn is connected to a balanced lever arm, and then weighting the end of the arm as required. The deflection of the lever (which depends on the depth to which the ball has penetrated into the rubber) is read by means of an optical device that greatly magnifies the displacement. To det. the plasticity of soft rubber, the same device is used to det. the rate of penetration of a cylinder of given diam. A. P.-C.

French rubber sponges. H. DE POIX AND F. DE POIX. *India Rubber World* **80,** No. 5, 69–70(1929).—A general description of present developments, with typical formulas. C. C. DAVIS

Who was the first to utilize rubber for erasing? A needed correction. MAX SPETER. *Gummi-Ztg.* **43,** 2270–1(1929).—Historical. Original references are cited to show that neither Priestley nor Magehaens was the originator of the idea of using rubber for erasing pencil marks. The credit should go to Nairne, a maker of mathematical instruments of London, who devised the eraser before 1770. C. C. DAVIS

The rational use of scrap and reclaimed rubber. H. BAUFARON. *Rev. gén. caoutchouc* **6,** No. 52, 14(1929).—Four formulas are suggested for molded products contg. scrap and reclaims. C. C. DAVIS

An inquiry into the use of reclaimed rubber. WALTER HUTCHINSON. *Déchets et Régénéres* **1,** No. 1, 5(1929).—The first of a series of articles to deal with the relative value of reclaimed and new rubber, the future of reclaimed rubber and the desirable properties

of reclaimed rubber, and to give representative mixts. in which reclaimed rubber is of special advantage. These points are covered briefly. C. D. DAVIS

Aging of rubber. B. V. BIZOV *Zhur. Prikladnoi Khim* **1**, 6–11(1928).—Soft grav rubber was cured in steam at 35 lb. per sq. in. for 10–60 min. and then aged at 70° for 24–96 hrs. The modulus of elasticity, the hysteresis, the product of these 2 quantities (or the "working capacity") and the swelling in AcOAm were detd. for individual samples and served to judge the degree of aging. The results obtained by these different methods were often contradictory. Properly vulcanized rubber undergoes smaller changes on aging than undercured rubber. The changes are probably due to a continuation of the vulcanizing process at the elevated temp. used in artificial aging tests. Artificial aging produces changes in rubber which are different from those observed in natural aging, and new accelerated testing methods must be developed which do not require an elevated temp. V. KALICHEVSKY

Laboratory apparatus for studying the aging and the vulcanization of rubber. R. FRIC. *Rev. gén. caoutchouc* **6**, No. 52, 9–10(1929); cf. *C. A.* **22**, 4876.—An app. for the O-bomb aging test and an app. for vulcanizing lab. samples are described and illustrated. The chief feature is the manner of heating, utilizing induced (Foucault) currents with the attendant hysteresis effects, the principle being the same as the Ribaud high-frequency method of heating furnaces. The cost of operation is economical and a sufficiently precise control of temp. is claimed. C. C. DAVIS

The outlook for synthetic rubber. OSCAR L. BRAUER. *J. Chem. Education* **6**, 1286–92(1929). E. H.

Organic accelerators of vulcanization. HAN TANAKA AND YOSHIYUKI HARA. *Repts. Imp. Ind. Research Inst. Osaka Japan* **10**, No. 1, 29 pp.(1929).—To make a comparative study of org. accelerators of vulcanization the authors tested the following: PhNHSCNHPh (I), PhN:C(NHPh)$_2$ (II), *p*-NOC$_6$H$_4$NMe$_2$ (III), aldehyde-ammonia (IV), *p*-C$_6$H$_4$(NH$_2$)$_2$ (V), (CH$_2$)$_6$N$_4$ (VI), HN:C(NHPh)$_2$ (VII) and C$_5$H$_{10}$NCSSH.C$_5$H$_{11}$N (VIII). The accelerator was mixed in the proportions of 0.25, 0.5, 0.75, 1.0, 2.0, 3.0, 4.0 and 5.0 per 100 of rubber mixt. The accelerating powers were in the order: VIII (0.25–0.5) (the figure indicates the amt. of accelerator used per 100 rubber mixt.), III (0.25–1.0), VII (0.5–2.0), V (0.5–3.0), VI (0.5–4.0), II (0.5–4.0), IV (0.75–4.0) and I (1.0–4.0). VIII is an ideal accelerator but needs careful attention in its treatment. VII is the best of all accelerators studied. F. I. NAKAMURA

The mode of action of organic accelerators of vulcanization. I. PAUL BARY. *Rev. gén. caoutchouc* **6**, No. 52, 3–8(1929) —An historical review and discussion of different types of org. accelerators. Tables giving the trade name, chem. compn., phys. state, d., odor, activity and manufacturers of 24 aldehyde-amines, 14 salts of thio acids, 5 guanidines and 10 miscellaneously classified compds. are included. C. C. D.

Action of adipic esters (Sipaline) on accelerators of vulcanization. Vulkan colors and rubber antioxidants. RUDOLF DITMAR WITH ALF MATHIESEN AND KARL H. PREUSSE. *Caoutchouc & gutta-percha* **26**, 14,618–20(1929); cf. *C. A.* **23**, 4098.—Tables show the soly. of various accelerators, Vulkan colors and antioxidants in isopropyl methyladipate, in dimethylcyclohexyl methyladipate and in methylcyclohexyl adipate and the characteristic fluorescent colors of Vulkan colors in ultra-violet light. C. C. D.

The influence of various accelerators on the surface vulcanization of rubber by ultra-violet radiation. RUDOLF DITMAR. *Gummi-Ztg.* **43**, 2325(1929).—By continuing expts. (cf. *C. A.* 23, 2602) it is shown that when ordinary activators are omitted from accelerated rubber mixts., ultra-violet radiation has itself an activating effect. This activation is accompanied by oxidation of the rubber, and this oxidation is more effective than the vulcanization, so that from a practical point of view satisfactory vulcanization is possible only when a red or a yellow protective pigment, *e. g.*, Se red, is added. With an activator like ZnO present in an accelerated mixt., ultra-violet radiation brings about vulcanization in a short time, so that the time must be carefully controlled to prevent oxidation, undercuring or overcuring. Ultra-violet radiation has the most favorable effect on rubber mixts. accelerated by tetramethylthiuram disulfide and contg. an activator. Surface vulcanization is complete in 4.5 min. without oxidation even in the absence of a protective red pigment. C. C. D.

The activating effect of various metallic oxides on the accelerating system piperidine pentamethylenedithiocarbamate and cyclohexylethylamine dithiocarbamate in the vulcanization of rubber in air. RUDOLF DITMAR AND ALF MATHIESEN. *Chem.-Ztg.* **53**, 479(1929).—The expts. are part of a study of the effect of metallic oxides on individual accelerators and on combinations of accelerators. From mixts. of pale crepe 100, colloidal S 3.5, piperidine pentamethylenedithiocarbamate 0.7, cyclohexylethylamine dithiocarbamate 0.7, "Agerite" 0.2 and metallic oxide or other compd. 10, in C$_6$H$_6$, films were prepd. by dipping and drying. These films were then cured in air

with a rise of 30 min. to 100° and 60 min. at 100°. The following data give the oxide or other compd., its activating effect, the appearance of the vulcanizate, and the condition of the vulcanizate, resp.: CaO, strong, transparent, very good (the best of all); Ca stearate, none, transparent, tacky; SrO, strong, transparent, supple and very good; Sr stearate, none, transparent, tacky; $SrCO_3$, none, milky, tacky; SrS, none, gray, tacky; SrO + Sb_2O_3 + wax, none, milky, tacky; BaO, considerable, transparent, good but somewhat tacky; MgO, none, opaque, tacky; ZnO, strong, opal, very good and tight; ZnS, none, transparent, tacky; $ZnSO_4.5NH_3$, strong, almost transparent, very good; CdO, considerable, brown-red, very supple and good; CdS, none, yellow, tacky; HgS, none, red, tacky; BeO, none, transparent, tacky; Al_2O_3, none, transparent, tacky; Fe_2O_3, hardly any, red-brown, tacky; Ni_2O_3, none, approaching transparency, tacky; Co_2O_3, none, black, tacky; MoO_3, none, opaque, tacky; SnO_2, somewhat, milky—glass-like, tacky; SnS_2, none, yellow-brown, tacky; Bi_2O_3, none, milky, tacky; Bi_2S_3, none, transparent, tacky; As_2O_3, considerable, transparent, good; Sb_2O_3, strong, orange-yellow, very good; Sb_2S_5, none, red, tacky; stearic acid, none, transparent, not vulcanized. It is considered that for this type of mixt., cured in air and required to be transparent, CaO and SrO are the best activators. C. C. DAVIS

The consumption of accelerator during vulcanization. L. v. WISTINGHAUSEN. *Rubber Age* (N. Y.) **25,** 261–4, 319–21(1929).—An English version of *C. A.* **23,** 3597. C. C. DAVIS

The utilization of vulcanized latex (Revultex). L. ST. *Gummi-Ztg.* **43,** 2325–6 (1929).—The chief disadvantages of dried vulcanized latex are its tendency to adsorb water and to swell in org. solvents. After contact with water, films of dried vulcanized latex are easily disintegrated by rubbing. Quant. tests, in which films of Revultex (prepd. 2 mm. thick by drying at 45–50° and then over H_2SO_4 to const. wt.) were swelled in water at 16.5–18.0° and the progressive increases in wt. during a period of 640 min. detd. are described. During the early stages adsorption was relatively rapid, *e. g.*, 6.8% after 90 min., while after 640 min. it was 12.5% and had not reached a max. C. C. D.

Report on the effect of different dilutions of latex and strengths of coagulant on the plasticity, vulcanizing and mechanical properties of rubber. ANON. *Trop. Agr.* (Ceylon) **71,** 36–9(1928).—Two sets of thin crepe were prepared from latex contg. 15 and 30% dry rubber, with varying proportions of AcOH, HCO_2H and Na_2SiF_6. Plasticity and vulcanization tests were made at the Imperial Inst. 6 mos. later. The results indicate that varying the concn. of the coagulant does not cause variation in plasticity or in vulcanizing and mech. properties. A. L. MEHRING

Time and temperature-plasticity relations for crude rubber as measured with the Goodrich plastometer. E. O. DIETERICH. *Ind. Eng. Chem.* **21,** 768–70(1929).—Quant. data are presented to show the applicability of the Karrer plastometer (cf. *C. A.* **23,** 4106) to raw rubber and to uncured rubber mixts., including the relative plasticities at 100° of different types of rubber after different periods of mastication, the relative plasticities of batches of pale crepe of different sizes at 100° after different periods of mastication, and the relative plasticities of masticated smoked sheets at various temps. (the temp. coeff.). C. C. DAVIS

The stretching and contracting of rubber lamella, the critical slipping temperature and its shifting by admixture. M. KRÖGER AND WAN-NIEN YAO. *Z. Elektrochem.* **35,** 358–62(1929).—It is shown that the unhindered inflation of rubber membranes to an approx. sphere represents a deformation especially favored by slipping. The energy increase in the case of the unhindered expansion of a sphere is as great as in longitudinal expansion. In spite of the difference of the outer deformation, the mol. processes accompanying the deformation are the same. The optical behavior also shows this. A crit. slipping temp. is obtained, which is shifted to a higher temp. by admixt. This gives a quant. measure of the "activity" of the added substance. R. I. RUSH

Early experiments with stearic acid in rubber compounding. W. F. RUSSELL. *Ind. Eng. Chem.* **21,** 727–9(1929).—See U. S. patent 1,467,197 (cf. *C. A.* **17,** 3808, 3809). C. C. DAVIS

Stearic and oleic acids as rubber-compounding ingredients. R. P. DINSMORE. *Ind. Eng. Chem.* **21,** 722–3(1929).—The expts. which are described show the relative effects of stearic acid and of oleic acid in representative rubber mixts., the influence of stearic acid on chem. and phys. vulcanization, and the different effects obtained with different accelerators. The most important function of stearic acid is to convert ZnO to a form which will react with the accelerator, aside from which it acts as a softener and as a retarder of chem. and phys. vulcanization. C. C. DAVIS

Effect of stearic acid on various crude rubbers. E. W. FULLER. *Ind. Eng. Chem.* **21,** 723–5(1929).—Since the total acid content of a rubber mixt. has considerable influence on the phys. properties of the cured mixt., uniform quality cannot be obtained by

the addn. of a const. porportion of stearic acid, because the stearic acid content of the raw rubber varies. Data show the phys. properties of different types of rubber mixts. contg. rubber with different total acid contents (detd. by the method of Whitby and Evans (cf. *C. A.* **22**, 3064), with and without the addn. of stearic acid. The effect depended not only upon the type of rubber, *i. e.*, upon the quantity of stearic acid furnished by the rubber, but also upon the other ingredients, particularly upon the accelerator. There is probably a well-defined state of acidity for each accelerator, and perhaps in turn for each combination of accelerator and other ingredients, which gives the best phys. properties of the resulting vulcanizates. This shows the importance of allowing for the natural acid content of the raw rubber in formulating mixts. which are to contain any desired proportion of stearic acid. C. C. DAVIS

Stearic acid in litharge-cured rubber compounds. J. R. SHEPPARD. *Ind. Eng. Chem.* **21**, 732–8(1929).—Expts. on the curing of different rubber mixts. with PbO under various conditions are described, and the quant. results are shown in graphs and tables. Though an org. acid is essential to vulcanization with PbO, smoked sheets usually contain a large enough proportion of natural org. acids for full activation. Rubber mixts. contg. PbO, mercaptobenzothiazole and gas black, of the character of tire treads, showed high tensile strengths over a wide range of cures, whether or not stearic acid was present. C. C. DAVIS

Effect of stearic acid on reclaimed rubber. H. A. WINKELMANN AND E. B. BUSENBURG. *Ind. Eng. Chem.* **21**, 730–2(1929).—Expts. are described which show the effect of stearic acid (1) in the heating process of the manuf. of reclaimed rubber; (2) as a plasticizing agent during the milling and refining of reclaimed rubber; and (3) on the properties of vulcanized rubber mixts. contg. reclaimed rubber. Stearic acid is far less effective than other softeners in its plasticizing action on vulcanized rubber scrap during devulcanization (in the alkali process because of its conversion into soap). On the other hand when added to devulcanized rubber on mills previous to the refining operation, it has a very beneficial effect by increasing the plasticity, by improving the tubing and calendering properties of mixts. contg. the reclaimed rubber, by reducing the "nerve" without producing tackiness, by improving molding properties, and by promoting the dispersion of fillers or pigments, thus improving the phys. properties of vulcanizates contg. the reclaim. In rubber mixts. contg. reclaimed rubber, stearic acid improves the vulcanization, diminishes the tendency to "blow" from reversion, and activates the acceleration with mercaptobenzothiazole. C. C. DAVIS

Effect of increased quantities of stearic acid on tread abrasions. C. OLIN NORTH. *Ind. Eng. Chem.* **21**, 725–6(1929).—The tensile strength and modulus at 300% elongation diminished progressively with increase in stearic acid, but the resistance to abrasion was greatest at 10–15% stearic acid and was greater with 30% stearic acid than with 2% stearic acid. A similar series with paraffin in place of stearic acid gave much the same results, showing that on the Graselli abrasion app. (cf. Williams, *C. A.* **21**, 2573) stearic acid has a lubricating action which renders a direct comparison with service on the road highly misleading. C. C. DAVIS

Adsorption of stearic acid by carbon. J. T. BLAKE. *Ind. Eng. Chem.* **21**, 718–9 (1929).—The theory of pigment reënforcement previously advanced (cf. *C. A.* **22**, 4876) is discussed further from a different point of view. Phys.-chem. calcns. based upon the assumption that the adsorbed mols. are dipoles and are adsorbed with a definite orientation indicate the validity of the theory, and that the dispersing agent is oriented on the surface of the filler particle. The center of the dipole axis is 4.2 A. U. from the surface of the filler, and since this is only 20% of the length of a stearic aid mol., the CO_2H group is the chief contributor to its dipole moment. The mechanism of the dispersion of fillers other than C black should be essentially the same. The theory explains the importance of fatty acids in the dispersion of pigments like C black in rubber. **Discussion.** C. R. BOGGS. *Ibid* 719.—A reënforcing pigment which is an elec. non-conductor is needed in the rubber industry for rubber insulation. There is also lacking a lab. test to det. the behavior of a filler or pigment in rubber, and particularly to det. the action of dispersing agents. Deflocculation of a kerosene paste of the substance by dispersing agents does not give comparable results. C. C. DAVIS

Patents

Rubber. RICHARD LATOUR. Fr. 651,530, Sept. 12, 1927. Waste rubber which has been vulcanized in the cold with CS_2 is recovered by shredding it to very thin sheets, removing the fatty substances, resins and S by sapon. with NaOH or KOH under steam pressure. Waste rubber which has been vulcanized by heating with free S is

reduced to a powder, oils, fats or other solvents such as crude rubber, acetone, ether, NH_3, chloroform, etc., are added and the mass is devulcanized with steam, shredded and treated as in the first case.

Rubber. THE ANODE RUBBER CO. (ENGLAND) LTD. Fr. 650,565, Mar. 7, 1928. Articles of rubber are made by bringing into contact with one another in a moist state and with or without pressure 2 or more pieces of material obtained directly by deposition, dipping, spreading, spraying or impregnating, from natural or artificial dispersions of rubber, etc., and drying or coagulating. Cf. *C. A.* **23**, 2850.

Rubber. THE B. F. GOODRICH CO. Fr. 648,759, Dec. 27, 1927. Conversion products of rubber are obtained by heating it for a long time with a solvent for rubber such as benzine, a phenol and one of the following: HCl, HBr, org. sulfonyl chlorides, org. sulfonic acids, dil. H_2SO_4 and trichloroacetic acid. The phenols include phenol, cresol, catechol, resorcinol, naphthols and *p*-chlorophenol. The products are plastic when heated and may be combined with fillers, pigments, etc.

Rubber. VEREINGTE ALUMINIUM-WERKE. A.-G. Ger. 472,662, Mar. 30, 1923. Glossy surfaces are produced on rubber goods by placing them on Al foil and rolling.

Treating rubber latex. J. MCGAVACK (to Naugatuck Chemical Co.). Brit. 298,628, Oct. 14, 1927. A reversible uncoagulated gel is formed by treating latex with an acid or, preferably, an alk. hydrosol of silicic acid in small quantity, either by direct addn. or by formation of the hydrosol in the latex. A gel which may be used for spreading, coating or other purposes forms in a few min. Examples and details are given.

Improving the aging properties of rubber. RUBBER GROWERS' ASSOCIATION, INC., G. MARTIN AND W. DAVEY. Brit. 299,585, Sept. 26, 1927. Latex serum and an alkali, such as NaOH, KOH or Na_2CO_3, are added to a rubber mixt. before vulcanization (suitably in a proportion of about 5% and 1%, resp., based on the quantity of the rubber in the mixt.).

Articles made from crude rubber. JAMES H. BURTON. Fr. 649,565, Feb. 22, 1928. Crude rubber (latex prima, crepes, etc.) is heated with stirring in an autoclave with an alk. soln., and the granulations obtained are similarly heated with water, dried and pressed in heated molds.

Rubber articles. THE NAUGATUCK CHEMICAL CO. Fr. 651,615, Dec. 30, 1927. Rubber articles are produced directly from latex by dilg. the latex, adding substances which enable the aq. portion to filter more easily through the deposit as it forms, agitating and heating. Raw latex may be used to which stabilizers such as glue, Na oleate, casein or undecylenic acid emulsion may be added, the solid contents of the latex being 8–24, preferably 14%. To render filtering easy a Zn oxide or salt and a sulfide of Na, K, Li or NH_4 are added, other substances which may be used are gel-forming colloids of buffer solns. controlling the H-ion concn., substances liberating metallic ions and vulcanization accelerators.

Compounding rubber with other materials. RAY P. DINSMORE (to Goodyear Tire & Rubber Co.). U. S. 1,712,333, May 7. An emulsion of rubber is mixed with a suspension of a filler material such as pptd. $BaSO_4$ and the rubber is coagulated on the filler, the product is washed free from water-sol. material and a rubber softener such as pine oil is added while the mass is still highly pasty and the product is then incorporated into a rubber mix upon the mill.

Deposition of rubber. THE ANODE RUBBER CO. (ENGLAND) LTD. Fr. 650,566, Mar. 7, 1928. In the elec. deposition of rubber from aq. dispersions, the uniformity of thickness of the deposit is influenced by screens of insulating or poorly conducting material such as hard rubber, or celluloid or of conductive material to form equi-potential surfaces. The screens may be perforated or cut away, and if sep. chambers are used the screens are preferably disposed in the cathode chamber. Cf. *C. A.* **23**, 2603.

Deposition of rubber. THE ANODE RUBBER CO. (ENGLAND) LTD. Fr. 650,977, Mar. 17, 1928. In the direct deposition of a substance of the nature of rubber on porous supports imbibed, *e. g.*, with a soln. of $CaCl_2$, or by electrophoresis, a coagulating agent is caused to act from the outside on the deposit before it is dried. This treatment may be given once or several times before the full thickness of the deposit is reached.

Deposition of rubber. THE ANODE RUBBER CO., LTD. Fr. 651,672, Aug. 3, 1927. In the deposition of rubber on an anode support from aq. dispersions thereof, particularly from natural latex, by an elec. current, protective colloids are added to the dispersion. Thus, 6–12 g. of soft soap is added to 1 l. of latex contg. 30% of rubber.

Deposition of rubber. WM. A. WILLIAMS. Fr. 650,326, Dec. 27, 1927. See Brit. 293,095 (*C. A.* **23**, 1527).

Apparatus for coating articles with rubber by electrodeposition, etc. G. F. WILSON (to Anode Rubber Co., Ltd.). Brit. 298,650, Oct. 13, 1927. Structural features.

Drying rubber deposits. A. Szegvari (to Anode Rubber Co., Ltd.). Brit. 298,483, Oct. 6, 1927. Articles formed by deposition of rubber from aq. dispersions are dried by applying to them a pervious material such as a fabric strip wrapping which exerts a compacting pressure. An app. is described.

Preserving rubber. B. D. Porritt, T. R. Dawson and Research Assocn. of British Rubber & Tyre Manufacturers. Brit. 299,169, Sept. 29, 1927. Rubber goods are coated with a mixt. contg. substances resistant to light and air, *e. g.*, a mixt. formed of soft "mineral rubber" 60, aldol α-naphthylamine 10, "Oil Red S" 2 and toluene 100 parts.

Recovery of rubber. Maurice dit René Gattefosse and Soc. française de produits aromatiques, Anciens établissements Gattefosse. Fr. 649,726, July 19, 1927. Vulcanized rubber is recovered by dissolving or treating it with an ester such as ethyl decylate, the alc. of which is not a solvent for rubber, and eliminating the ester by sapon. Cf. *C. A.* **23**, 732.

Artificial rubber. Katherine B. G. Edmondstone and Donald Chauvel. Australia 10,433, Nov. 16, 1927. Artificial rubber consists of cactus or other wax-like plants, with or without the leaves of vinca or periwinkle plant, white vinegar or AcOH and S.

Rubber substitute. Howard W. Matheson (to The Can. Electro Products Co., Ltd.). Can. 288,640, Apr. 9, 1929. The compn. specified includes clay, rubber, S, ZnO, coloring matter and a product made by treating vinyl ester with an aldehyde.

"Synthetic rubber." J. Baer. Brit. 298,889, Oct. 15, 1927. An aldehyde such as CH_2O is treated with alkali metal or alk. earth metal polysulfides in soln. with or without conjoint use of a halogen deriv. of a satd. hydrocarbon such as ethylene or methylene dichloride or dibromide. A rubber-like product is formed.

Making tires from synthetic rubber produced by polymerization of butadiene. I. G. Farbenind. A.-G. Brit. 299,037, Oct. 20, 1927.

Puncture-sealing composition. W. C. P. Tanner. Brit. 299,542, Aug. 9, 1927. Gum tragacanth which has been heated to at least 85°, water, CH_2O and a fibrous filler such as asbestos are used together. Carragheen and agar-agar may be substituted for part of the tragacanth.

Aldehyde-amine condensation products for use as rubber vulcanization accelerators. S. M. Cadwell (to Naugatuck Chemical Co.). Brit. 298,537, Nov. 1, 1926. Derivs. such as those contg. Cl, Br or I are formed from the condensation product of heptaldehyde and aniline or other similar condensation products of an aliphatic aldehyde having 2–7 C atoms and a primary amine. Various examples are given of the prepn. of different accelerators from these condensation products by use of halogenating and other reagents such as Cl, Br, I, acids, alc. and Na, HCl, Zn and Sn, etc. Cf. *C. A.* **22**, 3068.

Apparatus for vulcanizing tire flaps or other endless bands of rubber. D. S. Harrington (to Goodyear Tire and Rubber Co.). Brit. 299,005, Oct. 19, 1927.

Rubber vulcanization. J. Teppema (to Goodyear Tire and Rubber Co.). Brit. 298,942, Oct. 17, 1927. Accelerators are used comprising mercaptoxazoles or their derivs. such as reaction products with amines such as diphenylguanidine, diethylamine, butylamine and benzylamine (which may be prepd. by mixing solns. of the azole and the amine in hot alc.). Mercaptonaphthoxazole is prepd. by treating β-naphthol with HNO_2 to form a nitroso deriv., which is then treated with Na hydrosulfide and CS_2.

Vulcanizing rubber. J. Teppema (to Goodyear Tire & Rubber Co.). Brit. 298,622, Oct. 13, 1927. An accelerator is used which comprises the reaction product of a hydroxy aromatic aldehyde and an amine, *e. g.*, β-hydroxynaphthaldehyde and aniline may be heated under a reflux condenser to produce a yellow cryst. compd. which on heating gives off an oil and leaves a resinous residue which acts as an accelerator; or the aldehyde and amine may be heated for 1–2 hrs. in a closed vessel at 300° to form the accelerator.

Rubber. The Dunlop Rubber Co., Ltd. Fr. 652,439, Apr. 10, 1928. Viscous liquid or semi-solid accelerators, anti-aging agents, or softeners are mixed or combined with colophony before compounding them with rubber. Examples are given. Hardened rosin and substances such as ZnO or clay may be added to vary the consistency.

Recovery of latex from storage-tank settlings by centrifugal treatment. Aktiebolaget Separator. Brit. 299,808, Nov. 1, 1927.

Deposition of rubber. The Anode Rubber Co. (England), Ltd. Fr. 651,730, Mar. 24, 1928. The constitution of the electrophoretic deposition of rubber is acted upon by varying the content of electrolytes practically free from OH ions in the dispersion. Thus, the content of such electrolytes may be decreased by dialysis, or in-

creased by addn. of more of such electrolytes. Electrolytes, the anions of which form sol. or insol. compds. with the metal of the cathode, may be used. Cf. *C. A.* **23**, 3375.

Apparatus for mixing rubber compositions, etc. WILLET B. RANNEY (to Wm. Wrigley, Jr., Co.). U. S. 1,713,554, May 21. Structural features.

Rubber-mixing apparatus. RICHARD C. LEWIS (to Farrel-Birmingham Co.). U. S. 1,713,969, May 21. Structural features.

Apparatus for testing strength and stretch of rubber, etc. DAVID C. SCOTT (to Henry L. Scott Co.). U. S. 1,714,638, May 28.

Rubber articles. SOCIETÀ ITALIANA PIRELLI and UGO PESTALOZZA. Fr. 651,684, Jan. 27, 1928. Small quantities of solns. or suspensions of salts of bi- or tervalent metals are added to latex, which is subsequently heated to produce coagulation or thickening of the latex. Molded articles may be produced directly by dipping heated formers into the treated latex, or by heating the latex in a mold.

Thin-walled stretchable rubber articles. ISTVAN DOROGI and LAJOS DOROGI (one-half to Dorogi Es Tarsa Gummigyar R. T.). U. S. 1,713,751, May 21. See Brit. 288,541 (*C. A.* **23**, 731).

Rubber bulbs or other hollow articles. DUNLOP RUBBER CO., LTD., D. F. TWISS and E. A. MURPHY. Brit. 299,974, Oct. 5, 1927. A rod, tube, or like device carrying a bulbous enlargement of rubber having a roughened surface and of approx. the desired shape is dipped into a concd. dispersion of rubber or similar vegetable resins, followed by drying, and if desired by vulcanizing, and removal of the rod, etc. Successive dippings may be effected for increasing the thickness of the deposit, and a settling medium such as a heated soln. of $CaCl_2$ or NH_4OAc may be used. Brit. 299,975 specifies use of a distended collapsible former for use in a similar process. Cf. *C. A.* **23**, 1309.

Molded articles by dipping formers into rubber dispersions, etc. P. KLEIN and F. GABOR (to Dunlop Rubber Co., Ltd.). Brit. 299,737, June 28, 1927. In molding by dipping formers into dispersions such as those of rubber, gutta, balata, or mixts. of these, which may also contain proteins, cellulose esters, natural or synthetic resins, etc., the entire molds or their surfaces are formed of solid or solidified non-porous substances of such compn. that contact with the dispersion liberates agglomerating agents for the dispersion. The mold may be of a solid salt, such as an alum, which reacts with an alk. dispersion such as latex preserved with NH_3, or it may be of a metal, such as Zn or Al. Crystd. citric acid is mentioned, as are also liquid acids such as HOAc which may be solidified with collodion, and sol. salts which may be mixed with substances which are liquefiable by heat. The mold may have an inert skeleton. Emission of gas may be prevented by addns. to the dispersion or to the mold, *e. g.*, the mold surface may be formed from a paste contg. a metal such as Al bronze powder and an oxidizing agent such as MnO_2 or PbO_2. Metal molds may be coated with a film of gelatin to keep gas bubbles away from the deposit. The temp. may be raised to promote agglomeration. Cf. *C. A.* **23**, 1012.

Removing water from rubber-coated fabrics or other rubber products by electric endosmose. C. L. DARBY (to Anode Rubber Co., Ltd). Brit. 299,713, Oct. 28, 1927. Layers or articles of rubber or the like formed from an aq. dispersion are treated by elec. endosmose for removal of water. In one method described, a metal plate coated with rubber is connected as anode while immersed in Hg or an electrolyte; exposed parts of the plate not coated with rubber are coated with wax or other insulating substance. In another method, the coated plate, connected as anode, is placed between 2 metal plates connected as cathodes. An app. and various details of procedure are described. The process is adapted for treated wire or metal strip coated with rubber.

Rubber dressing or finish. JAMES S. MOTTER. U. S. 1,714,919, May 28. A mixt. is formed from xylene, "petroleum spirits," Al palmitate, black aniline oil dye, gilsonite, carnauba wax and barberry wax.

System of distributing fiber in rubber stock to form shoe soles, etc. WILLIAM B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,714,995, May 28. Relatively long fiber is distributed so as to reinforce the rubber in all directions in a sheeted material; the latter is plated so as to possess more extensibility in one direction than in another. Cf. *C. A.* **23**, 1528.

Rubber floor and wall coverings, etc. H. BECKMANN. Brit. 300,008, Nov. 8, 1927. Rubber floor or wall coverings and the like are coated with a thin film of porous or spongy rubber to facilitate their sticking to other materials by use of glue, pitch, resin, etc. The rubber article before vulcanization may be coated with viscous latex contg. S and vulcanization may be effected under conditions to prevent evapn. of water as described in Brit. 193,207 or the latex may contain substances which generate gas during vulcanization.

"Self healing" composition for automobile tire tubes. JOHN SCHWAB, JR. U. S.

1,715,213, May 28. Vulcanizing cement 30 and melted vulcanized rubber 30 parts are mixed with each other and then with honey 40 parts; the mixt. is heated to about 125°.

Synthetic rubber. ERNEST KLEIBER and PIERO GILARDI. Fr. 651,824, Mar. 27, 1928. Petroleum or its residues is oxidized with Na_2O_2 or for several days with HNO_3 after which it seps. into 2 layers, one composed of octanaphthenes, which on treatment with S are transformed to *m*-xylenes, and a turbid aq. layer, which is transformed by oxidation with fuming HNO_3 to cyclohexanes and passes to adipic acid. The *m*-xylenes are mixed with the adipic acid and they also are converted to adipic acid; terpenes are then added and after heating to about 150°, isoprene and butadiene are formed, from which artificial rubber is obtained.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 300,167, Nov. 7, 1927. Examples are given of processes such as described in Brit. 286,272 (*C. A.* **23**, 310) in which polymerization of hydrocarbons is effected in the presence of a colloid and an electrolyte, *e. g.*, in the presence of glue and Na_2SO_4 in an atm. of O.

Apparatus for vulcanizing rubber tires. F. KRUPP GRUSONWERK A.-G. Brit. 299,647, Jan. 19, 1928. Structural features.

Reclaiming vulcanized rubber. TATSUICHI TOKOYAMA. U. S. 1,714,835, May 28. The material is treated with a hydrogenated naphthalene rubber solvent contg. dissolved therein a substance such as NaOEt, which has a strong affinity for S.

Vulcanizing rubber. I. G. FARBENIND. A.-G. Brit. 300,208, Nov. 8, 1927. An alicyclic base or deriv. or compd. is used as a vulcanization accelerator. The basic group may be in the ring as in decahydroquinoline, decahydroquinaldine, or perhydromethylindol, or in non-cyclic combination as in hexahydromethyl toluidine. Various examples are given.

Vulcanization of rubber. THE RUBBER SERVICE LABORATORIES CO. Fr. 652,254, Apr. 5, 1928. See Brit. 297,726 (*C. A.* **23**, 2851).

Rubber vulcanization. THE RUBBER SERVICE LABORATORIES CO. Fr. 652,817, Feb. 6, 1928. Compds. produced by the action of one or more mol. proportions of an aldehyde, preferably of the aromatic series, on a compd. resulting from the reaction of one mol. proportion of an aliphatic aldehyde on 2 mol. proportions of a primary aromatic amine are used as vulcanization accelerators. Examples are given.

Rubber. ARNOLD R. F. VAN DER MARK and HEIN KREMER. Ger. 476,998, Apr. 23, 1925. Rubber objects are prepd. from freshly coagulated rubber, and their walls expanded by gaseous, liquid or solid pressure media and vulcanized.

Rubber latex. I. G. FARBENIND. A.-G. Fr. 33,927, July 25, 1927. Addn. to 630,983. Coagulation of latex is prevented by adding alcs., ketones or hydrocarbons or their derivs. and by adding neutral or alk. salts of acids such as diarylphosphoric and methylsulfuric acids. Latex with the addn. of suitable dispersing agents may be vulcanized with SO_2 and H_2S. Products having a basis of rubber and resins are prepd. by coagulating mixts. of alk. solns. of hydroxyaryl-formaldehyde condensation products and latex and hardening the product which seps.

Treating latex. VEEDIP, LTD. Fr. 652,695, Apr. 14, 1928. Latex contg. NH_3 is thickened by the addn. of a small quantity of ZnO, preferably in a finely divided state. The ZnO is made into a paste with water and a few drops of NH_3 and a little latex are added to produce a thick liquid which is added to the mass of latex. The latex is afterwards heated.

Rubber articles from latex. UGO PESTALOZZA (to Soc. Italiana Pirelli). U. S. 1,717,248, June 11. In forming tubes, sheets, gloves or other articles, there is added to latex such a quantity of $CaSO_4$ or other suitable coagulating agent as will coagulate the latex solely at a temp. of 70–100°, the latex is then brought in contact with a mold and is heated through the mold to effect coagulation; the coagulated latex is then dried.

Rubber articles. THE ANODE RUBBER CO., LTD. Fr. 653,215, Jan. 25, 1928. In the production of rubber articles on molds by dipping or electrophoresis, ultra-accelerators are used which effect the complete vulcanization of the articles during drying. Suitable substances are diethylamine dithiocarbamate, furoic acid and dithiofuroates and mercaptobenzothiazole. The vulcanization may be effected by heated air below 112°, or by dipping in hot water. An example is given. Cf. *C. A.* **23**, 2604.

Deposition of rubber. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 654,809, May 24, 1928. In forming deposits or coatings from suspensions, particularly of rubber, in liquids, gel-forming substances such as gelatin, agar-agar, carragheen moss, albumins or $ZnCl_2$ are added to the liquid. Electrolytes or coagulants may also be added. Deposits may be formed by several dippings, coagulation and drying taking place between each. Cf. *C. A.* **23**, 3598.

Electrodeposition of rubber or similar substances. W. A. WILLIAMS. Brit. 299,738, June 28, 1927. Deposition is effected by inserting a pair of electrodes of different materials (such as a Zn anode and a C cathode provided with a depolarizer) into a latex which contains an electrolyte such as NH_4Cl which does not readily cause coagulation and which will not evolve any substance deleterious to the latex or the deposit but will enter into chem. reaction with the anode and act as an excitant of elec. current. A voltage is used which is insufficient to decompose the added electrolyte and such that the total difference of potential between the electrodes is not sufficient to effect electrolysis of water. Fillers, vulcanizing agents and accelerators, etc., may be added to the latex. Cf. *C. A.* **23,** 3376.

Stabilizing rubber. SILESIA VEREIN CHEMISCHER FABRIKEN. Fr. 653,479, Apr. 26, 1928. Natural or artificial rubber is stabilized by the products of reaction of amines with polyhydroxyaldehydes such as sugar or with dissocn. products of polysaccharides, alone or mixed together or with other stabilizers, an accelerator being used at the same time. Products which may be used are, the reaction product of (1) glucose and α-naphthylamine, $PhNH_2$, *m*-toluylenediamine, urea or *m*-toluidine, (2) milk sugar and α-naphthylamine, (3) invert sugar and $PhNH_2$ or α-naphthylamine.

Rubber composition. ARTHUR BIDDLE (to United Products Corp. of America). U. S. 1,716,478, June 11. A coating compn. suitable for use also as *an insulating material*, sealing, making molded articles, etc., comprises rubber 10 lbs. (as contained in latex), dispersed in 100 lbs. of a mixt. of petroleum, castor and linseed oils and 75 lbs. of a casein glue soln. having a 20% casein content. Cf. *C. A.* **23,** 547.

Rubber composition. HERBERT A. WINKELMANN (to B. F. Goodrich Co.). U. S. 1,716,474, June 11. In reworking vulcanized scrap rubber, the comminuted material is masticated with a smaller proportion of crude rubber, admixed with pine tar and concd. H_2SO_4 and heated to cause a vigorous exothermic reaction.

Preserving rubber. ALBERT M. CLIFFORD (to Goodyear Tire & Rubber Co.). U. S. 1,717,093, June 11. About 1% of β-dinaphthol or other suitable substance of the general formula HO—R—R_1—OH, in which R and R_1 are naphthyl groups is added to rubber to render it more resistant to oxidation or aging. Cf. *C. A.* **23,** 2603–4.

Sponge rubber. REGINALD J. NOAR. U. S. 1,717,168, June 11. Fr. 655,020, May 31, 1928. See Brit. 284,938 (*C. A.* **22,** 4877).

Vulcanization of rubber. METALLBANK UND METALLURGISCHE GES. A.-G. Fr. 654,496, May 21, 1928. See Brit. 291,438 (*C. A.* **23,** 1309).

Rubber. MONTE L. CAMBERN, HERMAN O. LANGSTAFF and CHARLES J. STAPELFELD. Fr. 656,094, June 19, 1928. A crude rubber-like compd. or compd. suitable for addn. to rubber is obtained by distg. shale and condensing the vaporized portion. An app. is described.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 301,515, Dec. 2, 1927. 1,3-Butadiene or a homolog or analog may be polymerized in the presence of a water-sol. salt of a bile acid or deriv., which serves to accelerate the polymerization. Cf. *C. A.* **23,** 2071.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 655,785, Mar. 2, 1928.—See Brit. 286,272 (*C. A.* **23,** 310).

Rubber compositions. C. MACINTOSH & CO., LTD., S. A. BRAZIER and E. H. HURLSTON. Brit. 300,936, Aug. 19, 1927. In the manuf. of transparent or translucent rubber compns., a Zn or Cd salt of an org. fatty acid such as stearic, palmitic, oleic or linoleic acid is incorporated with the mixt. before vulcanization.

Rubber articles from dispersions. MERWYN C. TEAGUE (to Naugatuck Chemical Co.). U. S. 1,719,633, July 2. In forming gloves, toys or other articles, a form is repeatedly coated with a rubber dispersion and the dispersion is coagulated on the form. The coated form is washed after each coagulation operation and the coagulated rubber is subsequently dried on the form.

Rubber sheet material. DUNLOP RUBBER CO., LTD., R. F. MCKAY and W. H. CHAPMAN. Brit. 301,367, July 25, 1927. In the manuf. of rubber sheets or impregnated fabrics, a creamy deposit is formed electrophoretically from a suitable dispersion, partially dried if desired and then removed from the surface of the drum or like device on which the deposit is formed. Numerous details are given.

Perforated metal sheets, spools, etc., coated with rubber. ANODE RUBBER CO., LTD. Brit. 301,300, Nov. 26, 1927. The coating may be formed by dipping the metal sheet or article into latex which may be thickened and mixed with fillers, vulcanizing ingredients, etc. Electrophoresis also may be used for producing the coating after a preliminary coating of the metal with an easily oxidizable metal such as Zn to prevent gas formation. Various details are given.

Artificial rubber. I. G. FARBENIND. A.-G. Fr. 656,049, June 18, 1928. Masses resembling rubber are prepd. by polymerizing vinyl alc. in the presence of substances which increase the elasticity, particularly org. N compds. Examples are given of the polymerization of vinyl acetate in the presence of casein, albumin, glycocoll and benzoyl peroxide, or $C_{10}H_8$ and benzoyl peroxide.

Artificial rubber. I. G. FARBENIND. A.-G. Fr. 656,428, June 25, 1928. Rubber-like compds. are obtained by heating olefin hydrocarbons such as butadiene, isoprene or dimethylbutadiene with metallic oxides finely divided or sol. in colloids, such as PbO_2, MnO_2 and Ag_2O. Cf. *C. A.* **23,** 2603.

Artificial rubber. I. G. FARBENIND. A.-G. Fr. 655,217, June 4, 1928. The quality of artificial rubber from hydrocarbons is improved by a thorough mixing before vulcanization with finely divided C such as lampblack, active C or graphite. The C may be added to the hydrocarbons before polymerization. An example of both methods is given.

Artificial rubber. I. G. FARBENIND. A.-G. Fr. 655,456, June 7, 1928. See Brit. 292,103(*C. A.* **23,** 1528).

Rubber and like substances. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 655,535, June 8, 1928. Very viscous aq. dispersions of rubber, gutta-percha and balata are prepd. by adding polysaccharides, albuminoids or vegetable exts., which do not take a gel form even at high concn. Substances such as gelatin capable of forming gels may be added if hydrolyzed after addn. to a form incapable of gel formation, *e. g.*, by NH_3 or amines.

Electrophoretic deposition of rubber. DUNLOP RUBBER CO., LTD., and D. F. TWISS. Brit. 301,100, July 25, 1927. In electrophoretic deposition of rubber, balata or the like from natural or artificial dispersions, H ions are introduced as by adding HOAc in excess of that required for coagulation (coagulation being prevented) and the deposit is formed on a cathode or on a deposition base surrounding the cathode.

Rubber tubing. A. S. GREGG. Brit. 300,357, Sept. 27, 1927. Rubber tubing is provided with an external reënforcing of fabric and is then "doped" with a compn. such as one contg. cellulose acetate, nitrocellulose or a phenolic condensation product. The tubing is suitable for use for *carrying coal gas* and for various other purposes.

Rubber-working apparatus with a liquid-spray cooling system. F. H. BANBURY. Brit. 301,372, Nov. 28, 1927. Structural features.

Testing strength of rubber or other fabrics. F. SCHUBERT. Brit. 301,324, Nov. 24, 1927. Mech. features.

Coagulating rubber from latex. I. G. FARBENIND. A.-G. Brit. 300,719, Aug. 27, 1927. Proteases (such as those contained in succus caricae papayae) are used in the presence of addnl. substances facilitating the reaction or improving the properties of the rubber such as HCN, H_2S or saline mixts. having buffer properties. Air may be preliminarily passed through latex stabilized with NH_3 until a p_H of 8 is attained.

Preserving latex. I. G. FARBENIND. A.-G. Brit. 300,394, Nov. 18, 1927. The process described in Brit. 294,412 (*C. A.* **23,** 2071) is modified by the use, for preserving latex, of salts of sulfonic acids having tanning properties, of which several examples are given. Latex may be thus prepd., which is especially suitable for impregnating fabrics.

Preserving latex. I. G. FARBENIND. A.-G. Brit. 300,456, April 2, 1928. To latex preserved as described in Brit. 294,412 (*C. A.* **23,** 2071) or Brit. 300,394 (preceding abstract) by the salts of sulfonic acids having soap-like or tanning properties, there is added aliphatic or aromatic alcs. which may contain substituted halogens, ketones, hydrocarbons or halogen, nitro or amino substitution products of hydrocarbons such as heptyl alc., cyclohexanone, tetrahydronaphthalene or $PhNO_2$. The mixt. formed is stable and readily penetrates fabrics.

Treating latex. W. B. WESCOTT (to Rubber Latex Research Corp.). Brit. 301,077, Nov. 25, 1927. See U. S. 1,690,150 (*C. A.* **23,** 547).

Forming inner tire tubes, etc., by deposition from latex. SOC. ITALIANA PIRELLI. Brit. 301,476–7, Nov. 30, 1927. Mech. features.

Centrifuging rubber latex to remove suspended impurities. AKTIEBOLAGET SEPARATOR. Brit. 301,085, Nov. 24, 1927.

Rubber-surfaced pavements. HAZEL GROVE RUBBER CO., LTD., and T. GARE. Brit. 300,319, Aug. 19, 1927. Structural features.

Rubber vulcanization. J. TEPPEMA (to Goodyear Tire & Rubber Co.). Brit. 300,949, Nov. 21, 1927. A mercaptoarylthiazole in which at least one of the H atoms of the aryl ring is substituted, *e. g.*, 5-chloromercaptobenzothiazole, is made to react with an amine, aryl or aliphatic compd., *e. g.*, diphenylguanidine; the reaction product is used as an accelerator. Cf. *C. A.* **23,** 3376.

Vulcanizing rubber. RUBBER SERVICE LABORATORIES CO. Brit. 300,287, May 9, 1927. Vulcanizing accelerators are made by treating the condensation products of aldehydes and amines known as "Schiff's bases" or the aldehyde derivs. of such bases with an acid, neutralizing the acid and then reacting on the product with addnl. aldehyde or with CS_2. Examples are given.

Vulcanizing rubber to leather. LEON B. CONANT (to Standard Patent Process Corp.). U. S. 1,719,101, July 2. See Brit. 275,194 (*C. A.* **22**, 2292).

Steam-jacketted apparatus for vulcanizing rubber articles such as tires. JOHN R. GAMMETER (to B. F. Goodrich Co.). U. S. 1,719,218, July 2.

Cellular rubber. YVES CORNIC. Fr. 657,147, July 7, 1928. Substances capable of liberating CO_2, NH_3 or CH_4 are added to latex, which is then coagulated and vulcanized.

Rubber articles. ISTVÁN DOROGI, LAJOS DOROGI and DOROGI ÉS TARSA GUMMIGYAR R. T. Fr. 656,661, Jan. 27, 1928. Articles having thin walls are composed of one or more layers of rubber or the like and one or more layers of cellulose derivs. adhering to the rubber.

Rubber articles. Soc. ITALIANA PIRELLI. Fr. 656,473, June 26, 1928. Rubber articles are made direct from latex by the addn. to the latex of oxides or hydroxides of bi- or tervalent metals such as Zn, Mg, Ca, Al, assocd. with NH_4 salts. Cf. *C. A.* **23**, 3828.

Deposition of rubber. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 657,364, Feb., 21, 1928. Deposition of rubber-contg. liquid dispersion prepd. with vulcanized rubber such as rubber regenerated from waste rubber or like substitutes of natural rubber is obtained on permanent supports. The deposition may be carried out according to any of the processes described in Fr. 574,552, 638,504, 619,649, 632,144, 619,682, 628,296, 647,413 (*C. A.* **23**, 2603) or 647,232 (*C. A.* **23**, 2603).

Electrodeposition of rubber goods. PAUL KLEIN and ANDREW SZEGVARI (to Anode Rubber Co., Ltd.). U. S. 1,719,984, July 9. In effecting electrodeposition of solids from an aq. rubber dispersion on to a depositing backing such as a gypsum-coated anode, liquids are removed from the dispersion concurrently with the deposition of solids from it and modification of the effectiveness of the electro-osmotic action is effected by varying the relative pressures to which the dispersion and removed liquids, resp., are subjected. An app. is described.

Forming rubber tire tubes, etc., by deposition of superposed layers from thickened latex on a mandrel. W. B. WESCOTT (to Rubber Latex Research Corp.). Brit. 302,182, Dec. 10, 1927. Each layer is dried before the next is applied. An app. is described.

Crepe-rubber soles made from latex and containing an abrasive substance. Soc. FINANCIÈRE DES CAOUTCHOUCS. Brit. 301,900, Dec. 9, 1927. Different methods are described of forming shoe soles or tread material from latex and finely divided materials such as silica, pumice or carborundum.

Coating metals with rubber. A. JENNY. Brit. 302,250, Dec. 12, 1927. Metals such as Al, Zn, Fe or their alloys are coated by use of an alk. dispersion of rubber such as latex and an alk. soln. of stick lac or shellac, in an electrophoretic deposition process. Vulcanizing agents may be added to the dispersion.

Sheeting, strips and coatings of rubber. DUNLOP RUBBER CO., LTD., D. F. TWISS and E. A. MURPHY. Brit. 302,201, Aug. 12, 1927. A concd. unvulcanized rubber latex compn. in the form of a cream is spread upon a moving surface and subjected to heat to effect setting or gelling as quickly as possible (the setting in the case of manuf. of coated fabrics occurring before the water in the dispersion penetrates the fabric to any substantial extent). Compns. as described in Brit. 290,313 (*C. A.* **23**, 1012) or Brit. 219,635 (*C. A.* **19**, 750) may be used, with or without various specified fillers and compounding and auxiliary ingredients.

Bundle dipping process for coloring rubber bladders or toy balloons. JOHN C. GIBSON (to Pioneer Rubber Co.). U. S. 1,720,594, July 9. Mech. features.

Bonding rubber to metal surfaces. HAROLD GRAY (to B. F. Goodrich Co.). U. S. 1,719,930, July 9. Previous to assocn. of a rubber compn. with a metal surface such as steel and vulcanization of the rubber under pressure, the metal is pretreated with substances such as H_2SO_4, HNO_3, selenic acid, Se oxychloride, $SbCl_5$, $SbBr_3$, Cu_2Cl_2, FeF_3, Pb chromate, $HgCl_2$, Ni chloride, $POCl_3$, PCl_3, PCl_5, $AlCl_3$, $FeCl_2$, chlorosulfonic acid, $TiCl_4$, Co chloride, $CuCl_2$, Me_2SO_4, Et_2SO_4, C_2Cl_6, C_2HCl_5, benzotrichloride, benzyl chloride, CHI_3, naphthalene tetrachloride, benzenesulfonylchloride, or *p*-nitrobenzoyl chloride, which serve to promote good adhesion between the metal and rubber. Cf. *C. A.* **23**, 309.

Coating iron or other metal surfaces with rubber. F. AHRENS and HARZER ACHSENWERKE GES. Brit. 302,935, Dec. 21, 1927. The metal surface is first etched with

a strong acid and there is then applied (repeatedly if necessary) a soln. of rubber AmOAc with or without CCl_4, to which swelling agents may be added, and a sheet of rubber is finally pressed on to the prepd. surface and, if not already vulcanized, may be vulcanized *in situ*.

Rubber with variegated colorations. GUMMI- UND BALATAWERKE MATADOR A.-G. and F. GIRG. Brit. 302,102, April 2, 1928. Marbled, veined or streaked sheet material is formed by rolling or otherwise suitably working together portions of differently colored primary masses to which graded proportions of gas-forming and softening substances have been previously added. The primary materials may be partially vulcanized in order to secure sharper definition between the colors when they are combined.

Adhesive rubber composition. MERWYN C. TEAGUE (to General Rubber Co.). U. S. 1,719,948, July 9. See Can. 280,523 (*C. A.* **22**, 2856).

Preserving rubber. A. M. CLIFFORD (to Goodyear Tire & Rubber Co.). Brit. 302,271, Dec. 13, 1927. Aging qualities of rubber are improved by addn. of compds. such as β,β-dinaphthylamine or α,β-dinaphthylamine or other suitable secondary amines in which hydrocarbon radicals (preferably aryl) are of the same series. Details are given of the manuf. of the 2 compds. mentioned.

Preserving rubber. A. M. CLIFFORD (to Goodyear Tire and Rubber Co.). Brit. 302,144, Dec. 10, 1927. The "aging qualities" of rubber are improved by the addn. to the reaction product of an aromatic amine and an aliphatic acid or ester of such an acid, such as formnaphthalide, β-naphthylaminoaceto-β-naphthalide, naphthylmonoformamide of ethylenediamine or the reaction product of α- or β-naphthylamine and Et acetoacetate. Brit. 302,147 specifies the use of substances such as α-chloro-β-naphthol or α-amino-β-naphthol. Cf. *C. A.* **23**, 3828.

Preserving jelutong. BEECHNUT PACKING CO. Brit. 302,850, March 29, 1928. Coagulated jelutong is preserved from oxidation by treating it with Na or NH_4 primary or secondary phosphates or (less suitably) with NH_4 tartrate, sulfate, chloride or acetate.

Apparatus for stirring up dispersions particularly of rubber in water. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 656,660, Jan. 16, 1928.

Vulcanization accelerators. IMPERIAL CHEMICAL INDUSTRIES, LTD. Fr. 657,177, July 9, 1928. Dithiocarbamates and thiuram sulfides of morpholine and its C-substituted derivs. which are used as vulcanization accelerators are prepd. by treating morpholine or its C-substituted derivs. with CS_2.

Vulcanizing rubber. CLAYTON W. BEDFORD (to B. F. Goodrich Co.). U. S. 1,719,920, July 9. A polysulfide of a thioamine such as *N*-dithioaniline is used as a vulcanizing agent or an accelerator. Cf. *C. A.* **23**, 698.

Vulcanizing rubber. J. TEPPEMA (to Goodyear Tire and Rubber Co.). Brit. 302,142, Dec. 10, 1927. Vulcanization is accelerated by use of the reaction product of a 2-halobenzothiazole such as 2-chlorobenzothiazole and a dithiocarbamate such as Na diethyldithiocarbamate. The prepn. of the reaction product of 6-nitro-2-chlorobenzothiazole and Na diethyldithiocarbamate is also described and salts of piperidyl- and benzyldithiocarbamates, etc., also are referred to. Brit. 302,143 specifies the use as an accelerator of the reaction product of a benzoylnitrophenylsulfur halide such as 2-benzoyl-4-nitrophenylsulfur bromide and an alkali salt of an org. sulfide such as Na diethyldithiocarbamate. Cf. *C. A.* **23**, 4103.

Rubber vulcanization. S. M. CADWELL (to Naugatuck Chemical Co.). Brit. 302,176, Nov. 1, 1926. An accelerator is used comprising a hydrolyzed halogen-free deriv. of aldehydeamine condensation products from an aldehyde having a plurality of C atoms in open chain such as the condensation product from heptaldehyde and aniline. Cf. *C. A.* **23**, 1309.

Rubber vulcanization. WINFIELD SCOTT (to E. I. DU PONT DE NEMOURS & Co.). U. S. 1,721,057, July 16. A ditolylguanidine is used as an accelerator.

Rubber vulcanization. A. VOSHAGE. Brit. 301,802, Dec. 5, 1927. Vulcanizing molds are treated (suitably by spraying) with a soln. such as sugar and dextrin, to clean them and prevent formation of crust or scale.

Synthetic rubber. J. BAER. Brit. 302,399, Sept. 16, 1927. An elastic rubber-like product is obtained by the action of sulfides of NH_4 or alkalies or alk. earths as polymerization agents on satd. halogenated hydrocarbons such as methylene or ethylene dichlorides, dibromides or diiodides. Cf. *C. A.* **23**, 3376.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 302,733, Dec. 21, 1927. A mixt. is formed of various polymerization products of the same hydrocarbon of the butadiene type, such as various polymerization products of isoprene. Cf. *C. A.* **23**, 2324.

Rubber. THE ANODE RUBBER CO. (ENGLAND), LTD. (Robert F. McKay and Wilfred H. Chapman, applicants in England). Fr. 657,611, July 17, 1928. Rubber,

etc., sheets or coated or impregnated fabrics are made by obtaining a creamy deposit electrophoretically on a drum, etc., drying and removing. The aq. dispersion used preferably includes a protective colloid such as casein or gelatin in amt. greater than formerly used.

Rubber. I. G. FARBENIND. A.-G. Fr. 657,584, July 17, 1928. Rubber is pptd. from its latex by mixing it rapidly with acid, *e. g.*, HCl of such concn. that the p_H value of the mixt. is less than 2 and preferably less than 1. Substances which lower the surface tension may be added after the acid treatment.

Treating rubber latex. AKTIEBOLAGET SEPARATOR. Brit. 303,895, Jan. 13, 1928. The liquid poor in rubber obtained by dividing latex into 2 portions by centrifuging is centrifuged again to remove impurities before coagulating the rubber.

Electrodeposition of rubber from latex. S. O. COWPER-COLES. Brit. 303,214, Oct. 3, 1927. An app. is described having a perforated cathode arranged so as to permit any gas generated to escape through the perforations. Various structural details are described. Cf. *C. A.* **23**, 1309.

Electrodeposition of rubber together with sulfur. SAMUEL E. SHEPPARD and LEON W. EBERLIN (to American Anode, Inc.). U. S. 1,723,083, Aug. 6. Deposition is effected, from an admixture of a colloidal dispersion of S and an alk. aq. emulsion of unvulcanized rubber, in the form of droplets.

Electric deposition of rubber. IMPERIAL CHEMICAL INDUSTRIES, LTD., A. J. HAILWOOD, W. J. S. NAUNTON and A. SHEPHERDSON. Brit. 303,564, Oct. 7, 1927. In elec. deposition of rubber or the like from an aq. emulsion, there is added to the emulsion used an org. compd. adapted to form on oxidation at the anode a vulcanization accelerator. Na diethyldithiocarbamate, hydroquinone or a dimercaptan may be used. Leuco vat dyes, and other modifying ingredients also may be added.

Rubber deposition. DUNLOP RUBBER CO., LTD. and W. H. PAULL. Brit. 303,765, Oct. 7, 1927. Material for shoe soles or heels, tire treads, etc., is formed by electrophoresis or dipping from latex admixed with a viscose or oxycellulose soln., with fillers, vulcanizing agents, etc.

Rubber deposition. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 657,948, July 21, 1928. In the electrophoretic deposition of rubber or like substances from aq. dispersions, the dispersion is treated in such a way that the particles have a pos. charge, after which the deposition is carried out on a support mounted at the cathode. H_2SO_4 or AcOH may be used, and the H liberated may be fixed by using a cathode having an oxidizing action or by adding oxidizing substances to the dispersion.

Rubber tubing. DUNLOP RUBBER CO., LTD., D. F. TWISS and E. A. MURPHY. Brit. 303,546, Oct. 5, 1927. A core is passed (several times if desired) through an aq. dispersion of rubber, the coating is dried on the core, and the core may then be sepd. from the tubing formed by use of compressed air. Various details are given.

Mixing machine for treating rubber, etc. RICHARD C. LEWIS (to Farrel-Birmingham Co.). U. S. 1,721,962, July 23. Structural features.

Rubber facings on various surfaces. L. P. F. F. CRESSON. Brit. 303,400, Sept. 2, 1927. In applying rubber facings to cement or concrete floors, walls, table tops, etc., an excess of S above that required to form hard rubber is provided either in the base or in the rubber, so that a polysulfide is formed which permeates the interfacial surfaces and firmly unites the rubber to the cement. The cement may be mixed with various fibrous materials and the process is also applicable to materials such as felt or woven fabric impregnated with cement. Various details are given.

Freeing rubber deposits from water. DUNLOP RUBBER CO., LTD., E. A. MURPHY and D. F. TWISS. Brit. 303,544, Oct. 5, 1927. Various rubber deposits produced from either natural or artificial dispersions are treated, for removal of water, with a soln. of a salt or mixt. of salts such as NaCl, NH_4Cl, NH_4OAc, $CaCl_2$, alums or $MgSO_4$, with or without an acid such as HOAc or mixt. of acids or with fused substances which m. below 100° such as NaOAc or $Na_2S_2O_3$, acetamide, or NH_4 acetate or formate. Dehydration is effected by continuous penetrative osmotic action. Insol. or gelatinous thickening agents, etc., may be added to the solns.

Transparent vulcanized rubber. DUNLOP RUBBER CO., LTD., D. F. TWISS and E. A. MURPHY. Brit. 303,545, Oct. 5, 1927. Transparent vulcanized rubber is obtained without the use of a Zn activator by forming a deposit by electrophoretic or chem. means, or by dipping, spreading, coating, molding or extrusion from natural latex (which may be concd. in various specified ways) with addn. of S and of an "ultra accelerator" such as Zn dialkyldithiocarbamate, Zn piperidine carbothionolate or a Zn alkyl xanthate, with or without various stabilizing and softening agents, etc. The product may be vulcanized in boiling water or in a hot soln. of $CaCl_2$ or NH_4OAc used for removing water as

described in Brit. 303,544 (cf. preceding abstr.) and is finally treated in a 10% boiling NaOH soln. to remove free S and accelerator.

Rubber vulcanization accelerators. IMPERIAL CHEMICAL INDUSTRIES, LTD., W. J. S. NAUNTON and J. B. PAYMAN. Brit. 303,535, Aug. 31, 1927. Dithiocarbamates and thiuram sulfides of morpholine and its C-substituted derivs. which serve as accelerators are formed by treating morpholine or its C-substituted derivs. with CS_2. Examples are given of the production of Zn morphyldithiocarbamate, morpholine morphyldithiocarbamate, dimorphylthiuram disulfide, dimorphylthiuram monosulfide and dimorphylthiuram "tetrasulfide."

Vulcanization accelerators. AMERICAN CYANAMID CO. Fr. 657,807, July 18, 1928. Vulcanization accelerators are obtained by heating org. compds. contg. O with S and P. The S and P may be combined as P_2S_5, and the org. compds. may be of the aliphatic or aromatic series, preferably contg. OH groups such as BuOH or AmOH. Better results are obtained if a metallic oxide and a N compd. such as guanidine are also added. The reaction products are probably dithiophosphates.

Vulcanizing and preserving rubber. J. TEPPEMA (to Goodyear Tire & Rubber Co.). Brit. 303,827, Jan. 10, 1928. Reaction products of mercaptothiazoles with nitroso compds. (such as the reaction products of mercaptobenzothiazole with nitrosodimethylaniline or with nitrosonaphthol) are used as vulcanization accelerators and also serve to improve "aging qualities." Cf. *C. A.* **23**, 4376.

Timing and recording devices, etc., for rubber molding and vulcanizing apparatus. DUNLOP RUBBER CO., LTD., H. WILLSHAW, W. A. DAVIS and H. SMITH. Brit. 303,075, Aug. 22, 1927. Structural features.

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Tire Design With Relation to Comfort, Flexibility, and Wear

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THIS paper summarizes some of the more important factors in tire design which exert a controlling influence on tire comfort, flexibility, and wear. It is not attempted to add to any of the fundamental principles of tire design already laid down, but it is hoped to give a somewhat clearer insight into some of the simple mechanics and economics of tire behavior. In doing so, acknowledgment should always be made of the important and fundamental work of Schippel[1] and Healy[2], whose investigations have provided an exhaustive research into tire mechanics.

The scope of tire design is so broad that only a very few of the most important phases of it can be treated here. Several hundred specifications enter into the construction and composition of a single tire. Furthermore, the recognized types of tire failures are very considerable in number and may be due to either chemical or mechanical defects, or both. All normal tire failures, however, can be broadly classified as carcass failures, or wear failures, the chemical difficulties being included in both groups.

A perfectly balanced tire, correctly cured, will fail through tread wear, the carcass being designed to last somewhat longer than the tread. Normal carcass failures are due to the bending action or deflection which takes place with every revolution on the road, while tread failures are due in general to the abrasive action of the road.

Pneumatic tires are used on automobiles because they are resilient, and because they can deflect and prevent ordinary obstacles on the road from imparting an instantaneous vertical acceleration to the automobile wheels. This is due to the fact that a tire resembles, to a certain extent, a full elliptic spring. A comparison of the relative rates of deflection of a 6-inch tire and a 40-inch spring is shown in Plate 1. This indicates the relative absorption capacity of a tire at full inflation pressure and at 25 per cent. under-inflation.

Plate 2 shows what is meant by deflection, by percentage deflection, and by rate of deflection. The comfort of a tire

[1] "Fabric Stresses in Tires." *Ind. & Eng. Chem.* Nov., 1923.
[2] "The Tire as a Part of the Suspension System," *Auto. Eng.* Dec., 1924.

depends largely on its ability to absorb a given obstruction without an instant rebound, and there are two cases to consider. First, when the tire meets an obstruction at high speed, so that the obstruction is completely absorbed by the tire which reacts upward a fraction of a second later. Secondly, when the tire meets the obstacle at slow speed and although deflected, is almost instantly thrown in the air. To determine the impact effect on a tire passing an obstacle at high speed, the tire may be compressed on a plane surface under a normal load and the deflection noted. The obstacle is then placed in a series of positions under the tire, which is additionally loaded so as to maintain the same constant deflection that was present under normal load. The amount of additional loading required is obviously a direct measure of the upward force of the obstacle and is proportional to its height and shape.

The time required in passing the obstacle, multiplied by the average upward force of the obstacle, gives the impulse which is imparted to the wheel and which the automobilist is most anxious to avoid. In carrying out these experiments on different tires, it has been found that the upward reacting force—and therefore the upward impulse—is approximately the same regardless of the load or the tire size, provided the *rate of deflection under static load* is the same in each case.

In other words, the comfort of the tire itself, or its ability to withstand road shocks can be measured by determining its rate of deflection under static load. It further follows that a 30 by 3½-inch, high-pressure tire is substantially as comfortable for an automobile as a 6-inch balloon tire provided its rate of deflection under load is the same, and it can be made approximately the same by suitably regulating the inflation pressures. Of course, the tire life would be enormously decreased.

The effect on the axle of passing obstacles at low speed has been determined with various types of accelerometers and the comfort factor of different tires determined dynamically.

It is quite generally agreed that the disagreeable jarring sensations experienced in automobile riding are not due to the amount of vertical displacement of the wheels nor to the vertical velocity, but to the vertical acceleration. The human body, in other words, is very sensitive to changes in acceleration, and it is possible to accurately measure this discomfort effect by use of a seismograph attached to the axle, which gives the vertical displacements as the axle travels over the obstacle. See Plate 3.

From the vertical displacement (1) can be plotted the vertical velocity (2), which is the slope of the vertical displacement line. The vertical acceleration (3) or degree of discomfort experienced can further be plotted as the slope of the vertical velocity line as indicated. This represents an accurate dynamic method of measuring the comfort of a tire.

But it is interesting to note that it has been pointed out by Purdy and Day[8] that tires which have been classified as to comfort by the dynamic method almost invariably classify in exactly the same order when tested by the static rate of deflection tests.

Another important characteristic of a tire is its damping effect, or inability to recover completely from a given deformation. The damping effect can be measured by mounting the tire on a beam device and allowing the tire to fall, measurements being taken of the subsequent vibrations, and the damping factor being calculated as the log of the ratio of the successive amplitudes of vibration. Damping is a measure of the amount of work done on the tire during deformation which must be evolved in the form of heat. A tire with a high damping coefficient is naturally much more comfortable to ride on, but its life is cut down because of the damaging effect of flexing on the stiffer carcass construction, and the higher temperatures at which it is forced to operate. The cord tire came into general use simply because it was more resilient and efficient, although less comfortable than the fabric tire, which had a higher damping factor.

The tire maker is primarily interested in the per cent. deflection to which his tires will be subjected. The tire consumer, on the other hand, is primarily interested in the rate of deflection under load. Both, however, are vitally interested in the cost per mile. If a tire is inflated and then subjected to varying loads, it will be found that the per cent. deflection is nearly proportional to the load as shown in Plate 4. It will be noticed that at the lower inflation pressures the per cent. deflection increases at a faster rate with the load than with the higher pressures. The motorist has noticed this also and has found out that the high per cent. deflection obtained by lowering his inflation pressures means a rapid increase in the rate of deflection or comfort factor.

As previously pointed out, tire life is proportional, among other things, to the number and severity of the flexures to which the carcass is subjected, and that the severity of these flexures is proportional to the per cent. deflection at which the tire is operated.

It has been repeatedly demonstrated that for every percentage increase in carcass deflection above 12 per cent. there is a rapid and proportionate decrease in tire-carcass life. The money loss amounts to approximately $.001 per mile based on the present retail price schedules and on sizes ranging from 4.40 to 6.75. This loss is quite constant for the different sizes, and is due to the fact that the increased cost in the large sizes is offset by the decreased rate of deflection due to a 10-pound reduction in inflation pressure. Figures of this character apply only to high quality tires which are allowed to deliver full mileage. Rim width, tire diameter, tread contour, and number of plies, all have an effect on the

[8] *S. A. E. Jour., Mar., 1927.*

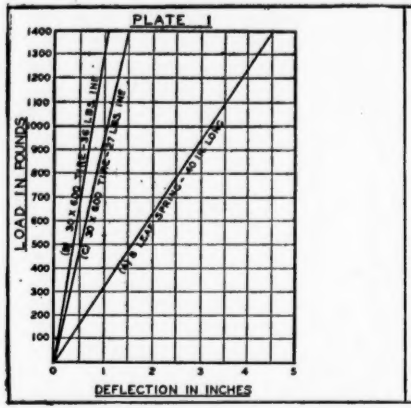
PLATE 1
LOAD IN POUNDS
DEFLECTION IN INCHES
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
1
2
3
4
5

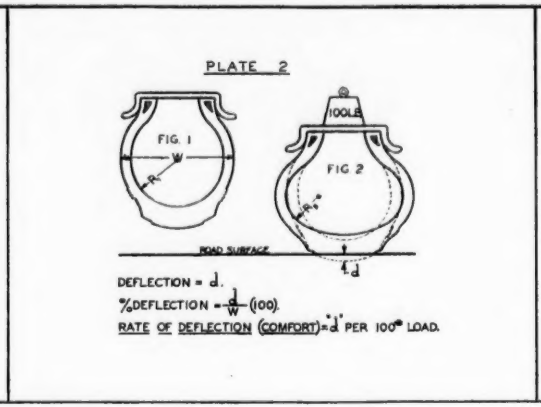
PLATE 2
FIG. 1
FIG. 2
100 LB
ROAD SURFACE
DEFLECTION = d.
%DEFLECTION = d/W (100).
RATE OF DEFLECTION (COMFORT) = d" PER 100# LOAD.

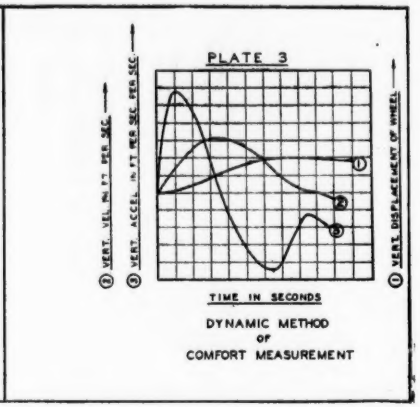
PLATE 3
TIME IN SECONDS
DYNAMIC METHOD
OF
COMFORT MEASUREMENT

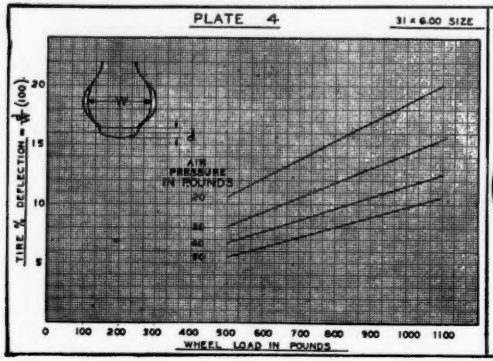
PLATE 4
31 x 6.00 SIZE
TIRE % DEFLECTION = d/W (100)
AIR PRESSURE IN POUNDS
WHEEL LOAD IN POUNDS
0
100
200
300
400
500
600
700
800
900
1000
1100
5
10
15
20

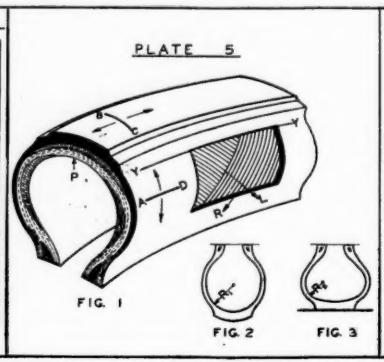
PLATE 5
FIG. 1
FIG. 2
FIG. 3

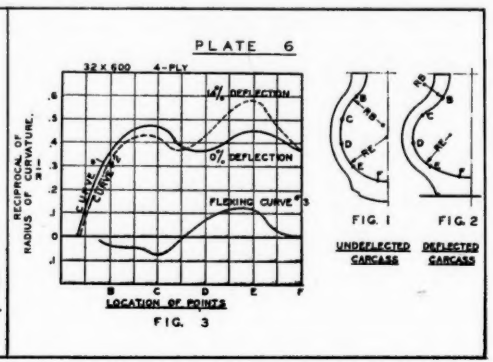
PLATE 6
32 x 600 4-PLY
1% DEFLECTION
0% DEFLECTION
FLEXING CURVE #3
RECIPROCAL OF RADIUS OF CURVATURE
LOCATION OF POINTS
FIG. 3
FIG. 1
FIG. 2
UNDEFLECTED CARCASS
DEFLECTED CARCASS

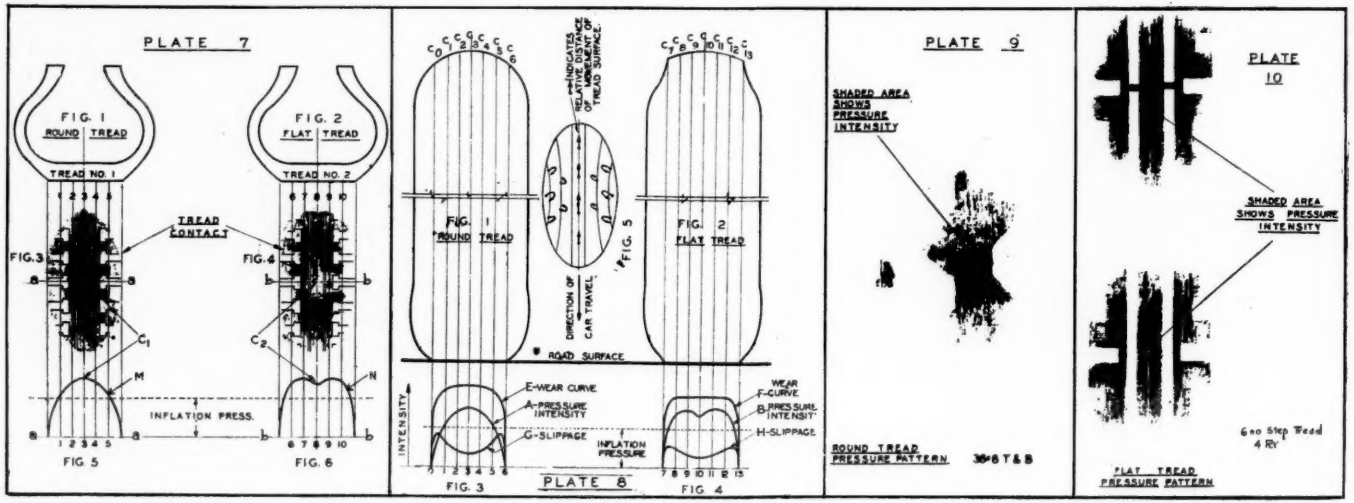
PLATE 7
FIG. 1
ROUND TREAD
FIG. 2
FLAT TREAD
TREAD NO. 1
TREAD NO. 2
TREAD CONTACT
FIG. 3
FIG. 4
INFLATION PRESS.
FIG. 5
FIG. 6
INDICATES RELATIVE DISTANCE OF MOVEMENT OF TREAD SURFACE.
FIG. 1
ROUND TREAD
FIG. 5
FIG. 2
FLAT TREAD
DIRECTION OF CAR TRAVEL
ROAD SURFACE
INTENSITY
E-WEAR CURVE
A-PRESSURE INTENSITY
G-SLIPPAGE
INFLATION PRESSURE
WEAR F-CURVE
B-PRESSURE INTENSITY
H-SLIPPAGE
FIG. 3
PLATE 8
FIG. 4
PLATE 9
SHADED AREA SHOWS PRESSURE INTENSITY
ROUND TREAD PRESSURE PATTERN
30×6 T&B
PLATE 10
SHADED AREA SHOWS PRESSURE INTENSITY
6 no Step Head 4 Rr
FLAT TREAD PRESSURE PATTERN

comfort; but a discussion of these effects is outside the scope of this paper.

We will now take up the question of tire-carcass failure and consider some of the stresses to which a tire is subjected. Reference to Plate 5 will make clearer the location of the most important stresses.

First, the inflation pressure tends to blow the tire apart along the transverse diameters such as *A D*, also along the cross-sectional diameters such as *B C*, as shown in Figure 1. These two stresses put the carcass cords in tension when the tire is inflated. The inflation pressure, however, must be corrected by the amount of pressure necessary to inflate the tube and this reduction in pressure tends to reduce the tension on the cords. The toroidal shape of the tire also has an effect on the transverse stress and tends to make it a maximum at point *P* in the tread center, gradually becoming less till it reaches a minimum at the beads. The stress intensities in the carcass can further be resolved into stresses acting along the individual cords, in direction *R* and in direction *L*, and after suitable corrections have been made for the count or number of cords per inch, the bursting stress can be calculated. It is, furthermore, possible to determine the different stresses in the different plies, and it will be found that the maximum bursting stress occurs on the inside ply at the crown of the tire at *P*.

Normal carcass failures are due, however, to the flexing or bending action which a tire undergoes when revolving on the road. A 30-inch tire, for example, will undergo 670 flexings during each mile of travel, or about 9,500,000 flexings during the tire life. Failure is eventually caused by the constant bending or flexing and by the constant fluctuation in cord tension in the carcass, as well as by the localization of the heat effects involved at the point of flexing.

During flexing on the road, an entirely new stress condition is set up, and this condition acts to increase the stress in certain zones in the cord carcass and to reduce it in certain other zones, as shown by the shaded area in the section. It is in this shaded area where the stresses continually vary from the normal, due to inflation to a minimum below inflation, that flexing trouble is most certain to occur. Carcass failures, other than accidental ones, therefore occur normally along the transverse circumference on the shoulder, at *Y*, where the greatest flexing takes place. Since the tension in some of the cords is actually lessened during the bending of the tire on the road, it would follow that carcass life is affected more seriously by the angle of bending of the individual cords than by the changes in carcass tension, although both exert an important influence.

In order to show graphically the bending action in the tire carcass as it revolves on the road, reference can be made to Plate 6. Figure 1 shows a half section of a normal uninflated carcass of a 32 by 6.00 tire and the letters

B, *C*, *D*, *E*, and *F* show the points on the interior of the carcass where the bending action takes place. The radius of curvature at each of these points is indicated as *RB*, *RE*, etc., as shown. Figure 2 shows the same carcass section in the deflected condition, and inspection shows that the various radii of curvature have undergone a change. Practically all the radii have become smaller, indicating a sharper curvature at points *C*, *D*, and *E*. In other words, the curvature at all points along the carcass has undergone a change due to bending, and it is the result of these repeated changes in curvature as the tire revolves which destroys the carcass.

It is possible to evaluate the degree of curvature at any point *B* in the carcass by taking the reciprocal of the radius at *B*, that is $\frac{1}{RB}$, and the points so obtained can be plotted as in Figure 3. In this plot the abscissae are the points *B*, *C*, *D*, *E*, and *F*, while the ordinates are the values of $\frac{1}{R}$ or the curvature. Curve 1 shows the degree of curvature at the different points along the undeflected carcass, and it will be noted that the greatest curvature occurs between *B* and *C*, or just above the bead, and again at *E* on the shoulder of the tire. Curve 2 shows the various curvatures of the deflected carcass when the carcass is at 14 per cent. deflection. It follows that the vertical difference between curves 1 and 2 represents the change in curvature between the undeflected and the deflected condition. We are able, therefore, to plot a third curve, 3, which shows this difference, and, therefore, shows the degree of flexing at all points in the carcass. At point *B*, just above the bead, the flexing is quite pronounced and gradually increases until *C* is reached. Flexing then decreases until between *C* and *D* it falls to zero. It then increases until point *E* is reached, where it is a maximum; then falls off to zero as *F* is reached.

A study of this flexing curve which should be plotted for all new tire designs is very interesting. It shows first of all that this particular carcass will fail close to point *E*, since this is the point of greatest flexing, and that the next weakest spot is close to point *C* as indicated. It is possible, through correct tire design, to modify the flexing to a considerable degree and to displace the maximum flexing toward a point where it will do the least harm; that is, where the carcass is thinnest as at *D*. A tire carcass which fails at *C* or above the bead shows radically poor design as flexing is readily displaced at this point, and should never equal the values reached at the shoulder where the tire meets the road. So much for carcass flexibility.

As previously pointed out, the normal tire fails through tread wear. This subject is still in the controversial stage, but it is hoped to indicate at least a basis for comparison of

the different factors which control abrasive wear. It is a reasonable assumption that tread wear, for a given tread compound and design, and for given road conditions and temperatures, is a function of: (1) The average pressure of the tread against the road. (2) The average tread slippage velocity. (3) The average distance of tread slippage.

In other words

$$\text{Rate of Wear} = K\left(\frac{\text{Slippage}}{\text{Velocity}}\right)(\text{Slippage distance})\ (\text{Pressure of Contact}).$$

This would seem to be borne out by the recent work of Lambourn[4], who reports wear as proportional to the (slippage)^2, and since the velocity equals the slippage distance divided by the time, the rate of wear on unit area of contact can be written

$$\text{Rate of Wear} = K\frac{(\text{Slippage})^2}{\text{Time}}(\text{Pressure Intensity}).$$

Since $\frac{1}{T}$ can be included in the constant, the wear should be proportional to the (slippage)^2 as shown by Lambourn.

To obtain a better picture of tread wear, it is therefore desirable to make an analysis of the pressure distribution and the slippage distribution on the tread surface exposed to the road, as shown in Plate 7.

When the tire is deflected on the road, the contact surface formed between the two is called the tread contact, and the character of this contact depends on the size and design of the tire as well as on the load and inflation pressure employed. It is, of course, on this area that tread wear takes place as the tire revolves on the road. Figures 3 and 4 are typical tread contacts for two distinct types of treads.

Since this tread-contact area supports the entire wheel load, it follows that the total pressure acting equals the load. It is, furthermore, obvious that if the tire were a very thin membrane, the pressure intensity over the entire pattern would equal the inflation pressure. Due, however, to the arch effect of the carcass and to the tread pattern or design, the pressure intensity varies as shown by the shaded areas in the diagrams.

Figure 3 represents the contact area formed by a rounded tread tire and Figure 4 the contact area formed by a flat tread tire, both tires being the same size and inflated to the same pressure.

In the case of tread No. 1, the pressure intensity increases from zero at the contact edges and reaches a maximum at C_1, the tread center, then falls off again to zero. This curious effect of pressure intensity distribution is due to the arch-

[4] "Methods of Determining Abrasion." *I. R. I. Trans.* Oct., 1928.

like support of the carcass, which in rounded tires tends to concentrate the pressure at the center of the pattern.

For the flat tread, the pressure rises from zero and reaches a maximum, then falls off at the tread center C_2. It then rises symmetrically and falls again to zero on the opposite contact edge. In a very flat tire or a very large tire it can be mathematically shown that the tread pressure at C_2 tends to approach the inflation pressure as a limit due to the absence of the arch effect of the carcass. Plate 9 shows an actual photograph made by deflecting a very rounded tread against heavy paper and the concentration of pressure at the tread center is very plain. Plate 10 shows a print of a flat tread taken in the same manner and the lessening of the pressure intensity at the tread center is very apparent.

It is possible, therefore, from an analysis of the pressure-intensity distribution shown in Plate 7, Figure 3 and Figure 4, to plot the average pressure intensities along the various sections—1, 2, 3, 4, and 5 in Figure 3, and 6, 7, 8, 9, and 10 in Figure 4, and this average for each tire is shown in Figure 5 as curve *M* and in Figure 6 as curve *N*. It will be noticed that the pressure potential for wear is very different in the two cases, being concentrated in the case of the round tread at the tread center, while in the curve of the flat tread it is midway between tread center and outside edges. The tread pressure intensity distribution is profoundly affected, however, by the tire size, the shape, distribution, and area percentage of the non-skid effect, and the carcass stiffness.

Having considered the effect of contact pressure between tire and road as one of the potentials for wear, we will conclude with a consideration of the slippage effects, which are brought out in Plate 8. This plate shows the round tread tire, Figure 1, and the flat tread tire, Figure 2, deflected against the road. Referring to Figure 1, C_0 to C_6 inclusive are the circumferences of the tire at various points on the tread surface, and Figure 2, C_7 tc C_{13} inclusive are the various circumferences of the flat tread tire.

A casual inspection of Figure 1 shows that there is a large difference in the circumferences at different parts of the tread. For example, C_0 and C_6 are much shorter than C_3. On a 30 by 6.00-inch tire this can amount to as much as 4 per cent. Now everyone knows that as a tire makes one revolution on the road, the car travels a distance equal to the rolling circumference of the tire. But what *is* the rolling circumference of the tire? Is it C_0 or C_3? If it is C_0, then the tread at C_3 must slip backward or drag by an amount equal to the difference between C_3 and C_0. Practically, a compromise is reached and the center of the tread drags a certain amount while the outer edges slip forward a certain amount. The slip along each one of the sections should be proportional to a factor which might be called the potential for slip.

While the forces acting along the different circumferences can doubtless be calculated and the distance and velocity of slip along each line established, we can refer to the recent work of Holt and Cook[5], who have determined the relative distances of slip along the different sections by means of waxed plates dusted with carborundum powder. Analysis of their pictures shows that the direction of slippage is as indicated in Figure 5 and proves that the distance of slippage for normal tractive effect is a maximum on the outside edges or shoulder and is about twice that at the tread center. The tread center drags while the shoulders move forward and many intricate lateral movements take place between the two zones of motion.

Under these conditions it is possible to represent the slippage by curve *G* in Figure 3 and as curve *H* in Figure 4. The difference in shapes of the two curves is due to the fact that there is less difference in the various tread circumferences on the flat tread tire. The total slippage is, therefore, decreased on this tread as compared with the rounded tread, but the ratio of center movement to edge movement is about one-half in each case.

If we apply an approximation of the wear formula suggested as a function of pressure times $(\text{slippage})^2$, the wear curve *E* for the round tread, Figure 1, and the wear curve *F* for the flat tread, Figure 2, can be drawn approximately as shown.

In conclusion, I wish to point out that the analysis of tread wear just suggested is not intended to be other than qualitative. It must be borne in mind that a new tire has certain potentials for wear along certain transverse sections, and that along certain of these sections wear will proceed very rapidly at the start. As these sections wear down, the pressure potential is shifted to other sections and the ultimate result is an equilibrium where the wear per unit area tends to become uniform on all sections in the contact area.

[5] "Measurement of the Tread Movement of Pneumatic Tires and a Discussion of the Probable Relation to Tread Wear." Research Paper No. 2 *Bu. Stand. J. R.*, July, 1928.

[*Reprinted from* INDIA RUBBER WORLD, *Vol.* 80, *No.* 3, *pages* 55-61. *June* 1, 1929]

Vulcanization Without the Use of Sulphur

Iwan Ostromislensky

AS far back as 1915 I described the various methods of vulcanizing rubber without the use of sulphur[1] which I was the first to discover. At the same time these researches gave rise to an international controversy in scientific circles[2]. For reasons beyond my control I have not until now been able either to publish the results of my physical or strictly technical tests of rubbers vulcanized by my new methods, or to place numerical valuations on their physical properties.

Many chemists who have repeated my experiments, of course under somewhat different conditions, often obtained results that did not coincide with mine. In consequence a number of discrepancies have gradually crept into the literature and in places even generalizations that are contrary to fact (C. Harries). Among others, B. D. Porritt[3] claims that 1.3.5. trinitrobenzene, although a vulcanizing agent for rubber, is inactive in the absence of oxides. This statement, as will be shown subsequently, is incorrect. Moreover, some of the experimenters have come to the conclusion that the vulcanization of rubber without sulphur cannot be applied practically in the rubber industry[4].

[1] *J. Russ. Chem.-Phys. Soc.*, 47, pp. 1,441, 1,453, 1,462, 1,467, 1,885, 1,904, (1915). For translations and reviews of these articles see *Chem. Abstracts*, 10, pp. 1,943, 1,946, 3,177, (1916); *Ibid*, 14, p. 235, (1920); *J. Chem. Soc.* 110-i, p. 278, (1916); *J. Soc. Chem. Ind.*, 35, pp. 59, 370, (1916); *Ibid*, 38, 955a, (1919); INDIA RUBBER WORLD, 54, pp. 410, 536, (1916); *Ibid*, 55, 65, (1916); *Ibid*, 61, 151, (1919); *India Rubber J.*, 52, pp. 467, 469, (1916); *Chem. & Met. Eng.*, 16, 161, (1917); *Caoutchouc & gutta-percha*, 13, 8,864, 8,888, 8,946; *Ibid*. 16, p. 9,701, (1919); *Ibid*, 20, p. 11,778, (1923); *Chem. Zentr.* pp. 774, 786, 911, 955, (1916); *Z. angew. Chem.*, 30, II, 48, (1916); *Gummi-Ztg.*, 30, 1,102, (1916); *Ibid*, 34, p. 275, (1920); *Chem.-Tech. Reportorium*, 40, 424, (1906); *Z. Untersuch. Leben.*, 38, 325, (1919); *Kunststoffe*, 12, p. 151, (1922). A more or less complete digest of my work will be found in Pearson's "Crude Rubber and Compounding Ingredients," p. 275, N. Y., 1918, and in B. T. Brook's "The Chemistry of Non-Benzenoid Hydrocarbons and Their Derivatives," p. 137, N. Y., 1922.

[2] H. P. Stevens, "Problems of Vulcanization by Nitrobenzene." *Caoutchouc & gutta-percha*, 13, 8,880, (1916); E. Buntschoten *Chem. Weekblad*, 15, 257, (1918); *Rubber Age*, 5, 291, (1919); *Chem. Abstracts*, 12, 1,518, (1918); *J. Chem. Soc.*, 114-i, 503, (1918); *Koiloid Z.*, 23, 25, (1918); INDIA RUBBER WORLD, 60, 559, (1919); *India Rubber J.*, 56, 719, (1918); *J. Chem. Ind.*, 2,119; *Z. angew. Chem.*, 31, II, 292, (1918); *Gummi-Ztg.*, 32, 692, (1918); *Chem. Zentr.*, 1918, I, 983; *Le Caoutchouc & gutta-percha*, 16, 9,765, 9,880, (1919).

[3] *India Rubber J.*, 52, (1916); *Chem. Abstracts*, 11, 223, (1917); *Scit. American*, 82, 374, (1916); *J. Soc. Chem. Ind.*, 35, 986, (1916).

[4] The Japanese experimenter, K. Sumitomo, on the contrary, used trinitrobenzene to vulcanize insulation for copper wire without applying sulphur. See Japanese patent No. 31,500, (1917). *Chem. Abstracts*, 12, 108, (1918). See also E. Hemming, "Plastic and Molded Electrical Insulation," p. 301, (1923), N. Y. Further, H. P. Stevens investigated the vulcanization of rubber cements by means of trinitrobenzene in the presence of MgO, PbO or the litharge product of a fatty oil.

Table I. Physical Properties of Rubber Vulcanized with 1.3.5. Trinitrobenzene.

Tensile is given in pounds per square inch. Set and stretch are given in inches. The first group of physical test figures under each experiment number indicates the results obtained twenty-four hours after curing. The second group of figures indicates the results obtained after aging.

The aging of the rubber was determined by heating the sample under test to 235° F. for three hours in a large steam-jacketed boiler, uniform temperature being maintained by a ventilator fan.

The tensile, set, and stretch of the vulcanizates recorded were tested with a Scott apparatus using dumb-bell form test pieces.

Experiment No.	1	2	3	4	5*	6	7	8*	9	10	11
Rubber, pale crepe	100	100	100	100	100	100	100	100	100	100	100
1.3.5. Trinitrobenzene	2	2	2	2	1	4	6	2	2	2	2
Aniline	1	0	0	0	0.2	1	1	1	1	1	1
Zinc oxide (Kadox)	150	150	150	150	150	150	150	150	100	...	...
Litharge	...	...	...	...	...	...	...	...	...	30	60
Sulphur	...	...	2	8	...	...	...	...	...	...	...
Minutes of cure	25	30	25	30	...	45	75	...	75	30	15
Tensile	3665-2500	3209-2560	2745-2755	2730-2325	...	1400	735	...	2345-1675	2260-1310	2515-1310
Set	0.17-0.18	0.2-0.2	0.17-0.22	0.35-0.32	...	0.04	0.1	...	0.12-0.08	0.05-0.05	0.08-0.1
Stretch	7.8-6.8	7.2-5.9	7.6-7.7	7.9-6.7	...	5.0	4.3	...	6.4-5.8	7.0-6.5	8.4-6.2
Minutes of cure	30	60	30	60	...	...	90	...	90	60	20
Tensile	3520-2215	3280-2390	2730-2975	2860-2695	...	...	593	...	2920-1980	2275-1230	2410-1240
Set	0.2-0.15	0.18-0.15	0.22-0.22	0.42-0.32	...	...	0.06	...	0.14-0.11	0.06-0.06	0.09-0.08
Stretch	7.6-6.5	6.1-5.5	7.4-7.0	7.1-6.7	...	...	4.5	...	6.7-6.2	7.0-6.5	8.3-6.0
Minutes of cure	35	120	40	120	...	...	...	...	105	...	...
Tensile	3450-2410	3130-2285	2785-2610	2450-1590	...	...	...	...	2895-1980	...	...
Set	0.2-0.17	0.22-0.15	0.21-0.19	0.44-0.18	...	...	...	...	0.18-0.11	...	...
Stretch	7.6-6.6	6.0-5.7	7.3-6.9	6.5-4.6	...	...	...	...	6.8-6.3	...	...
Minutes of cure	40	25	...	...	...	...	...	...	120	...	...
Tensile	3600-2270	3035-2390	...	...	...	...	...	...	2625-1870	...	...
Set	0.19-0.18	0.20-0.16	...	...	...	...	...	...	0.12-0.11	...	...
Stretch	7.6-6.6	6.4-6.7	...	...	...	...	...	...	6.5	...	...
Minutes of cure	...	20	...	...	...	...	...	...	...	...	...
Tensile	...	3025-2510	...	...	...	...	...	...	...	...	...
Set	...	0.18-0.21	...	...	...	...	...	...	...	...	...
Stretch	...	6.6-6.3	...	...	...	...	...	...	...	...	...

5. Undercured in 180 minutes.
8. This stock in a mold placed in a constant temperature oven cured completely in 5 hours at 95° C. An uncured product is obtained in 17 hours at 50° C.

Experiment No.	12	13	14	15	16	17	18*	19	20	21	22
Rubber, pale crepe	100	100	100	100	100	100	100	100	100	100	100
1.3.5. Trinitrobenzene	2	2	2	2	2	2	2	2	2	2	2
Aniline	1	1	1	1	1	1	1	1	1	1	1
Litharge	100	...	...	...	...	...	...	...	...	...	...
Magnesium oxide	...	20	30	50	75	...	...	...	...	...	...
Carbon black	...	...	...	...	...	175	...	...	...	...	...
Kieselguhr	...	...	...	...	...	...	10	20	30	40	50
Minutes of cure	5	75	75	75	50	30	90	90	90	30	60
Tensile	1045-1090	1710-510	1545-1070	1485-1085	1315-740	955-885	1570-420	2000-840	1690-1360	2130-1642	3170-2240
Set	0.07-0.1	0.14-0.05	0.09-0.07	0.10-0.08	0.12-0.10	0.14-0.14	0.05-0.04	0.05-0.05	0.05-0.07	0.09-0.08	0.09-0.07
Stretch	6.3-5.2	8.7-6.8	7.3-7.1	7.6-6.2	5.8-5.1	4.2-4.3	6.9-5.1	6.1-5.0	5.5-5.3	6.4-5.7	5.2-4.4
Minutes of cure	15	90	90	90	75	...	105	105	105	45	90
Tensile	1910-965	1913-790	1760-995	2120-1102	1355-1116	...	1525-430	1880-905	2205-1220	2205-1720	3445-2085
Set	0.09-0.09	0.08-0.07	0.08-0.08	0.10-0.08	0.10-0.10	...	0.03-0.01	0.08-0.05	0.06-0.04	0.1-0.09	0.1-0.08
Stretch	6.4-5.4	8.4-6.8	8.7-6.9	8.7-6.5	6.0-5.9	...	6.5-5.3	6.1-5.3	6.0-5.0	6.3-5.8	5.2-4.1
Minutes of cure	25	105	105	105	90	...	120	120	120	60	105
Tensile	1650-910	2110-290	1910-1155	1925-1255	1390-975	...	1612-340	1760-780	2225-1370	2105-1975	3295-1880
Set	0.10-0.06	0.08-0.04	0.07-0.10	0.12-0.09	0.10-0.10	...	0.07-0.01	0.05-0.05	0.09-0.06	0.09-0.09	0.05-0.06
Stretch	5.8-5.3	8.5-5.0	8.8-6.8	7.7-6.5	5.9-5.6	...	6.7-4.6	6.0-5.1	5.9-4.8	6.3-5.6	4.9-3.9
Minutes of cure	35	120	...	...	105	...	160	...	...	90	...
Tensile	1105-645	2200-475	...	...	1275-940	...	...	...	...	2350-1785	...
Set	0.07-0.07	0.07-0.04	...	...	0.10-0.10	...	...	...	...	0.1-0.09	...
Stretch	5.3-4.6	8.6-6.3	...	...	5.7-5.4	...	...	...	...	6.0-5.3	...
Minutes of cure	...	...	...	...	...	...	...	...	...	105	...
Tensile	...	...	...	...	...	...	...	...	...	2370-1585	...
Set	...	...	...	...	...	...	...	...	...	0.09-0.06	...
Stretch	...	...	...	...	...	...	...	...	...	6.1-5.2	...

18. Badly overcures in 160 minutes.

Table I—Continued

Experiment No.	23*	24	25	26	27*	28*	29*	30*	31*	32*	33
Rubber, pale crepe	100	100	100	100	100	100	100	100	100	100	100
1.3.5. Trinitrobenzene	2	2	5	2	2	2	1	0.5	0.3	2	2
Aniline	1	0	1	1	1	1	0	0	0	1	1
Litharge	...	...	...	...	...	30	30	30	30	32	25
Carbon black	...	100	100	120	155	100	100	100	100	35	30
Kieselguhr	100	...	...	...	...	...	...	...	...	...	...
Minutes of cure	30	20	60	60	...	5	30	30	60	15	30
Tensile	2300-2230	2140-1830	2025-1690	2374-1945	...	1970-1565	1635-1425	1590-1335	...	2450-1985	2575-1655
Set	0.12-0.1	0.18-0.2	0.09-0.03	0.17-0.1	...	0.13-0.11	0.09-0.1	0.12-0.12	...	0.15-0.17	0.07-0.1
Stretch	3.4-3.7	4.0-3.7	2.4-2.3	3.3-2.8	...	3.5-3.0	2.7-2.6	3.1-2.9	...	5.0-4.8	4.9-4.4
Minutes of cure	20	30	90	90	...	10	45	45	...	30	45
Tensile	2470-1985	2265-1760	1890-1595	2210-2110	...	2360-2415	1735-1575	1330-1635	...	2020-1775	2830-1615
Set	0.19-0.16	0.11-0.11	0.05-0.04	0.13-0.11	...	0.05-0.06	0.1-0.09	0.1-0.13	...	0.1-0.07	0.1-0.09
Stretch	4.2-3.8	3.6-3.1	2.1-2.0	3.1-2.7	...	2.7-2.8	2.9-2.5	2.7-3.1	...	4.7-4.0	5.3-4.1
Minutes of cure	60	60	105	...	...	20	60	60	...	45	60
Tensile	2450-2010	2265-1905	1875-1370	...	...	2525-2435	1585-1285	1430-1425	...	2055-1410	2695-1630
Set	0.07-0.09	0.08-0.08	0.15-0.05	...	...	0.04-0.07	0.1-0.04	0.12-0.12	...	0.11-0.07	0.11-0.11
Stretch	3.3-2.9	3.1-2.8	2.2-2.1	...	...	2.7-2.6	2.5-2.3	2.7-2.7	...	4.4-3.8	5.0-4.9
Minutes of cure	105	...	...	...	...	...	...	...	...	...	...
Tensile	2105-1990	...	...	...	...	...	...	...	...	...	...
Set	0.07-0.08	...	...	...	...	...	...	...	...	...	...
Stretch	2.8-2.9	...	...	...	...	...	...	...	...	...	...

23, 28, 29, and 30. These stocks may be used for the production of leather substitutes. They present beautiful, shining black non-blooming surfaces.

27. Vulcanization complete in 5 minutes at 141° C. The products are very hard and brittle. They cannot be removed from the mold without injury. They have no stretch, set, or trace of elasticity. The maximum of carbon black that can be milled into rubber is 155 per cent by weight.

28. Vulcanization of this mix for 10 days at room temperature yields a product giving the following physical tests: tensile, 905-1220; set, 0.54-0.19; stretch, 4.8-3.0.

31. Overcures at 60 minutes at 141° C.

32. All cures reported are overcures. This stock will cure at room temperature in about 40 hours.

Experiment No.	34*	35	36	37	38	39*	40	41*	42	43	44
Rubber, pale crepe	100	100	100	100	100	100	100	100	100	100	100
1.3.5. Trinitrobenzene	2	2	2	2	2	2	2	2	2	2	2
Aniline	1	1	1	1	1	1	1	1	1	1	1
Litharge	30	30	60	10	5	30	30	30	30	...	...
Magnesium oxide	...	...	...	...	...	...	...	...	...	5	10
Carbon black	10	20	10	10	5	...	...	...	...	30	30
Carborundum	...	...	...	...	...	...	...	20	20	...	...
Graphite	...	...	...	...	...	130	20	...	...	...	...
Minutes of cure	5	5	5	5	45	10	15	75	5	30	75
Tensile	2704-1332	2770-1877	2121-1582	2160-1186	2098-1063	1485	2100-1592	1550-555	1780-885	2737-1750	2810-1765
Set	0.11-0.09	0.1-0.11	0.12-0.08	0.06-0.04	0.05-0.04	0.26	0.12-0.11	0.09-0.06	0.13-0.12	0.11-0.07	0.08-0.11
Stretch	6.7-5.6	6.1-5.5	6.7-6.0	6.5-5.6	6.3-5.5	5.3	6.8-6.4	6.5-6.0	8.0-7.1	6.2-5.2	6.4-5.2
Minutes of cure	10	10	10	10	60	25	35	...	15	45	...
Tensile	1866-915	2600-1664	2431-1515	2630-1071	2396-815	1180-920	2105	...	1400-630	2735-1700	...
Set	0.07-0.07	0.1-0.06	0.09-0.08	0.07-0.03	0.06-0.03	0.25-0.24	0.12	...	0.10-0.09	0.09-0.06	...
Stretch	6.0-5.1	6.0-5.1	6.6-5.6	6.4-5.2	6.7-5.1	4.9-4.7	6.5	...	7.5-6.4	5.9-5.2	...
Minutes of cure	15	15	15	20	75	...	...	...	30	75	...
Tensile	1445-710	3080-1895	2345-1330	2500-1154	2100-610	...	...	...	1380-365	2315-1700	...
Set	0.09-0.05	0.12-0.11	0.1-0.07	0.1-0.04	0.05-0.02	...	...	...	0.08-0.04	0.1-0.06	...
Stretch	5.4-4.2	6.5-5.4	6.2-5.5	6.4-5.3	6.2-5.0	...	...	...	7.1-4.8	5.4-4.6	...
Minutes of cure	...	30	30	30	90	...	...	...	45	90	...
Tensile	...	2370-1635	1705-1630	2225-1265	1840-650	...	...	...	1000-350	2620-1670	...
Set	...	0.12-0.09	0.07-0.08	0.08-0.06	0.04-0.03	...	...	...	0.08-0.05	0.1-0.05	...
Stretch	...	5.5-4.6	5.7-5.6	6.6-5.3	5.9-5.1	...	...	...	6.3-4.9	5.3-4.7	...
Minutes of cure	...	45	...	60	...	...	...	...	...	105	...
Tensile	...	2135-1475	...	1225-365	...	...	...	...	...	2450-1935	...
Set	...	0.1-0.07	...	0.05-0.03	...	...	...	...	...	0.1-0.06	...
Stretch	...	5.5-4.6	...	5.3-3.3	...	...	...	...	...	5.2-4.8	...
Minutes of cure	...	60	...	...	...	...	...	...	...	120	...
Tensile	...	2345-1275	...	...	...	...	...	...	...	2000-1590	...
Set	...	0.07-0.03	...	...	...	...	...	...	...	0.09-0.05	...
Stretch	...	5.0-4.7	...	...	...	...	...	...	...	5.6-4.5	...

*

34. Cures of 15 minutes and over are overcured.
39. Vulcanization complete in 2 minutes at 141° C.
41. Overcured. The carborundum was too coarse. Individual sharp particles of it cut the vulcanizate when the latter was stretched giving too low tensile tests.

Table I—Continued

Experiment No.	45	46	47*	48	49	50	51	52*	53*	54*	55*
Rubber, pale crepe	100	100	100	100	100	100	100	100	100	100	100
1.3.5. Trinitrobenzene	2	2	2	2	2	2	2	2	2	2	2
Aniline	1	1	1	1	1	1	1	1	1	1	1
Litharge	...	...	30	30	60	10	30	5	10	...	...
Magnesium oxide	20	20	...	...	...	...	...	...	...	...	...
Carbon black	20	35	...	...	...	...	30	2	2	100	...
Kieselguhr	...	...	30	50	30	60	30	5	5	20	...
Cadmium sulphide	...	...	...	...	...	...	...	...	...	...	75
Minutes of cure	60	90	40	10	5	60	10	10	25	60	180
Tensile	2435-1365	2790-2430	2430-2145	2705-2020	2565-2040	2950-2165	3120-2435	2515-1425	2060-1545	2285-1865	1690-1309
Set	0.11-0.07	0.16-0.1	0.17-0.14	0.24-0.2	0.2-0.17	0.26-0.09	0.22-0.19	0.08-0.07	0.10-0.01	0.14-0.12	0.12-0.1
Stretch	6.3-5.0	5.4-5.1	6.2-5.9	7.1-5.9	6.6-6.3	5.3-5.2	5.6-5.1	7.6-6.7	6.3-6.0	3.3-2.8	7.5-6.8
Minutes of cure	...	105	60	15	10	75	15	25	40	90	160
Tensile	...	2805-2355	2380-1425	2735-2000	3020-2405	2825-1970	3310-2460	1810-1320	2230-1325	2220-2070	...
Set	...	0.15-0.1	0.12-0.11	0.2-0.16	0.2-0.18	0.23-0.19	0.19-0.16	0.07-0.04	0.09-0.07	0.12-0.11	...
Stretch	...	5.4-5.1	6.2-5.3	6.7-5.5	7.1-6.1	5.4-5.0	5.3-5.1	6.2-5.8	6.2-5.5	2.9-2.8	...
Minutes of cure	...	120	...	20	15	90	30	40	55	...	...
Tensile	...	2635-2138	...	2395-1780	2835-2540	2795-2285	2985-2400	2125-1265	1580-1420	...	...
Set	...	0.1-0.1	...	0.21-0.2	0.17-0.19	0.23-0.23	0.21-0.18	0.06-0.06	0.08-0.06	...	...
Stretch	...	5.0-4.8	...	5.8-5.7	6.7-6.2	5.3-5.3	4.9-5.0	6.5-5.8	5.8-5.9	...	...
Minutes of cure	...	...	...	25	...	105	...	...	...	...	...
Tensile	...	...	...	2990-2500	...	2795-2280	...	...	...	...	...
Set	...	...	...	0.22-0.2	...	0.24-0.21	...	...	...	...	...
Stretch	...	...	...	6.4-5.7	...	5.3-5.3	...	...	...	...	...
Minutes of cure	...	...	...	55	...	...	...	...	...	...	...
Tensile	...	...	...	2560-2270	...	...	...	...	...	...	...
Set	...	...	...	0.2-0.21	...	...	...	...	...	...	...
Stretch	...	...	...	5.9-5.6	...	...	...	...	...	...	...
Minutes of cure	...	...	...	70	...	...	...	...	...	...	...
Tensile	...	...	...	2490-1805	...	...	...	...	...	...	...
Set	...	...	...	0.21-0.2	...	...	...	...	...	...	...
Stretch	...	...	...	5.8-5.1	...	...	...	...	...	...	...

47. A driving belt made of this stock proved better, and more durable in service than one made of sulphur cured stock.
52 and 53. These stocks were used successfully for the production of rubber cements in benzene on black tire tread stocks. It remains to be determined if this solution will become altered in time at room temperature, for example, by coagulating.
54. Leathery quality. Compare stocks 23 to 31.
55. Undercured in 160 minutes at 141° C.

Experiment No.	56	57	58	59	60	61*	62*	63	64*	65	66
Rubber, pale crepe	100	100	100	100	100	100	100	100	100	100	100
1.3.5. Trinitrobenzene	2	2	2	2	2	2	2	2	2	2	2
Aniline	0	0	0	0	0	0	0	1	1	1	1
Zinc oxide (Kadox)	0	0	50	20	50	...	120	...	...	...	100
Litharge	...	...	...	...	+50g. HgS	...	...	30	30	30	...
Magnesium oxide	5	30	...	...	...	...	...	...	...	...	...
Carbon black	...	...	...	...	...	...	...	...	...	...	20
Aluminum oxide	...	...	...	...	...	...	...	...	...	30	...
Silica	...	...	...	...	...	...	...	...	30	...	...
Kieselguhr	...	...	...	...	...	...	...	30	...	...	...
Calcium sulphide	...	...	...	...	...	100	...	...	...	...	...
Cadmium sulphide	75	75	75	75	...	...	...	...	...	...	...
Minutes of cure	30	10	45	...	45	...	75	5	5	...	20
Tensile	2730-2225	2640-2130	1695-1220	...	1175-500	...	1600-1700	1895-1455	2300-1725	...	3210-2845
Set	0.11-0.12	0.13-0.14	0.12-0.10	...	0.12-0.08	...	0.1-0.1	0.20-0.19	0.08-0.12	...	0.17-0.18
Stretch	7.2-7.7	6.9-7.3	6.3-5.9	...	7.9-7.1	...	4.4-5.2	7.1-7.1	7.7-7.6	...	6.6-6.3
Minutes of cure	45	15	60	45	60	...	...	10	10	...	35
Tensile	2530-1585	2245-1760	1925-1640	1860-1615	1870-825	...	...	2020-1440	2195-1355	...	3210-2750
Set	0.10-0.11	0.11-0.10	0.13-0.11	0.13-0.13	0.11-0.09	...	...	0.17-0.20	0.09-0.10	...	0.18-0.16
Stretch	7.1-7.2	6.4-6.2	6.6-6.6	7.5-7.6	8.3-7.4	...	...	6.8-6.9	7.5-6.8	...	6.1-5.8
Minutes of cure	...	30	...	60	75	45	...	20	15	15	50
Tensile	...	2465-1520	...	1835-1645	1885-960	1295-1105	...	1560-1380	1650-1290	1445-850	3395-2780
Set	...	0.11-0.08	...	0.11-0.12	0.11-0.08	0.16-0.16	...	0.13-0.15	0.09-0.07	0.12-0.14	0.25-0.17
Stretch	...	6.4-5.9	...	7.3-7.0	8.0-7.0	6.5-6.3	...	6.1-6.2	6.6-6.6	7.9-7.4	6.4-5.6
Minutes of cure	...	...	...	120	90	60	...	30	20	20	60
Tensile	...	...	...	1790-1740	1225-1025	1215-1075	...	1540-1125	1750-1035	1530-900	3300-2585
Set	...	...	...	0.12-0.15	0.10-0.07	0.13-0.14	...	0.15-0.14	0.08-0.07	0.12-0.13	0.15-0.13
Stretch	...	...	...	7.7-7.7	6.9-7.1	6.2-6.3	...	6.5-5.8	6.8-6.2	7.8-7.4	6.2-5.6
Minutes of cure	...	...	...	...	120	75	...	40	30	30	90
Tensile	...	...	...	...	2065-815	1190-900	...	860-405	765-403	1685-980	3140-2637
Set	...	...	...	...	0.09-0.06	0.14-0.16	...	0.1-0.09	0.08-0.06	0.13-0.14	0.13-0.13
Stretch	...	...	...	...	8.0-7.0	6.3-5.8	...	5.1-3.0	5.4-4.4	7.7-7.3	5.0-5.0
Minutes of cure	...	...	...	...	160	...	...	60	...	...	...
Tensile	...	...	...	...	1510-1065	...	...	520-475	...	...	...
Set	...	...	...	...	0.10-0.08	...	...	0.06-0.04	...	...	...
Stretch	...	...	...	...	7.4-7.2	...	...	3.8-3.7	...	...	...
Minutes of cure	...	...	...	...	120	...	...	...	...	...	...
Tensile	...	...	...	...	1460-900	...	...	...	...	...	...
Set	...	...	...	...	0.08-0.07	...	...	...	...	...	...
Stretch	...	...	...	...	7.5-7.3	...	...	...	...	...	...

*

61. Badly overcured in 105 minutes at 141° C. 62. Badly overcured in 90 minutes at 141° C. 64. Badly overcured in 40 minutes at 141° C.

Table I—Continued

Experiment No.	67	68	69	70	71	72	73*	74	75	76	77
Rubber, pale crepe	100	100	100	100	100	100	100	100	100	100	8.1-6.1
1.3.5. Trinitrobenzene	2	2	2	2	2	2	2	2	2	2	100
Aniline	1	1	1	1	1	0	1	1	1	1	2
Zinc oxide (Kadox)	100	50	100	100	50	100	20	20	40	...	1
Litharge	...	...	20	50	...	...	...	20	...	30	...
Carbon black	10	20	...	...	...	...	22	20	50	...	30
Chromic oxide	...	...	...	...	...	...	...	...	...	30	...
Stannic sulphide	...	...	...	...	...	...	...	...	...	...	...
Kieselguhr	...	...	...	...	100	40	20	20	50	...	50
Colophony	...	...	...	...	...	...	...	...	10	...	...
Minutes of cure	30	30	15	10	60	35	30	10	60	5	...
Tensile	2715-2220	2710-1376	2805-2075	2945-2385	2225-2425	2855-2455	1015-835	2395-2250	1860-1385	1795-1105	10
Set	0.13-0.11	0.1-0.07	0.13-0.12	0.18-0.14	0.43-0.26	0.29-0.24	0.12-0.09	0.19-0.16	0.28-0.3	0.09-0.11	1390-730
Stretch	6.6-6.3	6.3-5.2	6.3-6.1	6.3-6.3	5.1-4.7	6.2-5.8	5.0-5.2	5.7-5.6	5.2-5.3	7.5-7.1	0.13-0.11
Minutes of cure	45	45	30	15	75	60	60	15	90	10	7.9-6.4
Tensile	3190-2230	2715-1187	2905-2005	2995-2330	2575-2375	3115-2300	2775-...	3125-2415	2030-1500	1865-1055	15
Set	0.16-0.2	0.09-0.05	0.13-0.1	0.15-0.13	0.39-0.3	0.30-0.24	0.14-...	0.2-0.18	0.29-0.29	0.11-0.08	1295-820
Stretch	6.9-5.9	5.9-4.8	6.3-5.9	6.3-5.7	5.0-4.6	6.0-5.0	6.2-...	6.0-5.4	5.0-5.2	7.4-6.6	0.09-0.11
Minutes of cure	60	60	45	25	90	75	90-...	30	105	25	7.6-6.5
Tensile	2405-2175	2845-1940	2760-2300	2350-2310	2530-2285	3055-2695	3250-2485	2895-2310	2080-1745	1270-1205	30
Set	0.13-0.18	0.11-0.09	0.1-0.09	0.12-0.14	0.37-0.29	0.28-0.2	0.11-0.14	0.2-0.15	0.26-0.24	0.06-0.08	1334-865
Stretch	5.9-5.8	6.3-6.1	5.4-5.8	5.7-5.6	4.4-4.3	5.9-5.5	5.6-5.6	5.4-5.1	5.3-5.0	6.3-6.4	0.12-0.10
Minutes of cure	75	75	...	35	105	90	...	...	...	40	7.4-6.2
Tensile	2890-2355	3020-1955	...	2320-2095	2610-2360	3095-2645	...	...	...	1640-675	45
Set	0.15-0.09	0.17-0.11	...	0.11-0.12	0.42-0.29	0.29-0.26	...	...	...	0.08-0.05	960-755
Stretch	6.6-5.9	6.8-5.1	...	5.1-5.2	5.3-4.3	6.0-5.7	...	...	...	6.8-5.9	0.14-0.08
Minutes of cure	...	90	...	...	...	105	...	...	...	...	8.1-6.1
Tensile	...	2405-1640	...	...	...	3125-2450	...	...	...	...	...
Set	...	0.12-0.08	...	...	...	0.3-0.25	...	...	...	...	...
Stretch	...	5.7-5.2	...	...	...	5.7-5.6	...	...	...	...	...
Minutes of cure	...	105	...	...	...	...	...	...	...	...	...
Tensile	...	2430-1425	...	...	...	...	...	...	...	...	...
Set	...	0.09-0.05	...	...	...	...	...	...	...	...	...
Stretch	...	5.8-5.2	...	...	...	...	...	...	...	...	...

73. All tests made of this stock on a 90-minute cure, including flexing test and abrasion in unit time, etc., were almost the same as those of the sulphur containing sample of black tire tread. The vulcanizate is a little softer and under a blow shows proportionally greater elastic property. For this reason a black tread was made from it.

Experimenters Set Right

I would begin by pointing out that most of the writers who applied my methods made the fundamental mistake of using too much of the vulcanizing substance. For example, in many instances they applied 1.3.5. trinitrobenzene (TNB) to the amount of 6 to 8 per cent., whereas it should never be used in quantities exceeding 3 per cent. (better even 2 per cent.) on the weight of the rubber. Further, all rubbers vulcanized with TNB should contain protective agents to prevent oxidation and aging. As such protective agents, a comparatively large amount of various oxides (PbO, ZnO, etc.) may be used, or else a certain amount (about 0.3 to 1.0 per cent.) of aromatic amines, such as aniline, or naphthylamines, etc.

TNB-Cured Product Superior to Sulphur-Cured

The object of the present article is to point out that rubber which has been vulcanized without the use of sulphur in the correct way is a very valuable product, particularly from a practical standpoint. Not only is it so good as rubber that has been vulcanized with sulphur, but it often displays more valuable physical properties as compared with the latter. It seems to me that every specialist who looks through the tables attached to this article carefully and from an unbiased point of view must agree that the "oxygen" vulcanization of rubber discovered by me is in all respects on a par with the classical sulphur-cured rubber that was discovered by Charles Goodyear in 1839.

As to the mechanism of the vulcanization of rubber, it seems to me that the different observations which I have made in the course of many years' work have in all respects corroborated the theory which I expounded in 1915 and which has been reviewed in many of the English and American journals. In his article entitled "Ueber Aggregation und Desaggregation" the German scientist Harries[5] says: "Auf die Beziehung zwischen meinen Untersuchungen und denen Ostromyslensky's ist merkwuerdigerweise niemand aufmerksam geworden."[6] On this question I still maintain my former point of view and I have no doubt whatever that there is not a single point in common between my observations and my theory and those of Harries.

Production of TNB

In the experiments described in this article in Tables I and II, we used as a vulcanizing substance almost exclusively symmetrical (1.3.5.) trinitrobenzene, which I shall hereafter designate for brevity's sake by the letters TNB. We pro-

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[5] *Ber. Deut. Chem. Ges.*, 56, p. 1,051, (1923). In this article Harries maintains that I consider vulcanization, as such, to be a process of oxidizing rubber. Nowhere did I make this assertion.

[6] In translation: "So far nobody has yet, wonderful to say, remarked upon the connection between Dr. Ostromislensky's and my investigations."

duced this substance, in accordance with the data we found in the literature, by splitting off carbon dioxide from the corresponding trinitrobenzoic acid in an aqueous solution; the latter we obtained in turn by oxidizing trinitrotoluene (which is a very cheap product, especially in post-war times,) by means of chromic acid. Among other things we succeeded in greatly simplifying the technical phases of this well-known process and were also able to obtain a higher yield of TNB.

We would mention that although TNB is ignited by an open flame, yet it only flashes but does not explode. Of course, a blow with a hammer as well as pulverization of TNB in a mortar will not cause any explosion either. TNB does not detonate at the explosion of mercuric fulminate. It detonates only when this substance explodes in the presence of tetryl. It follows that TNB is not dangerous as far as explosibility is concerned.

Toxicity of TNB

As to the toxicity of TNB, it is far less toxic than aniline or even benzene. When carefully and properly handled, especially in the pulverization stage, TNB, to my knowledge, never once caused any case of dermatitis or of any other skin disease among the chemists or hands working in this line. But in those cases where it was handled without gloves or where its dust was inhaled, it has been known to bring on the symptoms of TNB poisoning, (local swelling of the skin, rashes, erythema, itching, and other symptoms, such as irritation of the mucous membrane of the eyeball.)

These, however, quickly yielded to treatment. As a rule we rubbed the affected parts several times a day with a 0.5-1.0 per cent. solution of potassium permanganate. All the symptoms of TNB poisoning disappeared quickly and completely. After we had put into practice the method of carefully preparing on the mill a master batch of rubber and TNB, and using this as the vulcanizing agent in the place of pure TNB, we never had any more cases of TNB poisoning either among the chemists or the workmen.

Advantages of Using 1.3.5 Trinitrobenzene

1. Vulcanizates cured with 1.3.5. trinitrobenzene (TNB) do not age so rapidly as those cured with sulphur. They are considerably more durable in use as well as when stored. Their homogeneity is far greater. We still have a sample of a TNB vulcanizate made in Moscow in 1916. This sample has remained unchanged for thirteen years and its constants appear to be like those of the fresh vulcanizate. No solid surface either of a brittle or tacky character has been formed.
2. TNB promotes more rapid vulcanization.
3. Certain compounds with TNB vulcanize perfectly at ordinary temperature, that is, at 50° or 100°C.
4. Vulcanization with TNB facilitates the introduction

into the rubber mixture of various substances, which, if treated with sulphur, would decompose such, for instance as many organic dyestuffs, leather waste, ground sawdust, woodflour, etc.

5. The different compounds of rubber and TNB are proof against over-vulcanization. A mixture of 100 rubber, 150 zinc oxide, 2 TNB, and 1 aniline, after vulcanization lasting 20 minutes at 141°C. (40 pounds), displays almost the same constants (tensile, set, stretch) as after vulcanization lasting 120 minutes at 141°C., thus showing that no noticeable over-vulcanization has occurred even when the time of cure has been six times longer. The same conditions prevail when using admixtures of kieselguhr, carbon black, etc.

6. When vulcanizing rubber with TNB, various new filling agents, such as carborundum and silicon, may be included in the mixing. They act as good accelerators on the one hand, and on the other, they often produce most interesting new physical characteristics in the vulcanizate.

7. Vulcanizates treated with TNB frequently show better physical characteristics, such as: elasticity under pressure (measured by the height of rebound of a metal ball), tensile, and set, which are superior to those of sulphur-cured products.

8. The surface of rubber vulcanized with TNB under the requisite conditions stays without any visible change, when stored, for a very considerable time. For example, it retains its gloss and color unchanged and in a uniform condition. On the contrary, the majority of rubbers vulcanized with sulphur begin rather speedily to liberate this sulphur either in the form of spots or crystals on the surface, or more often in the form of a fine dust or bloom which covers the whole article.

9. Rubber vulcanized with TNB displays greater resistance to acids and is less apt to decompose after being in contact with metals, copper for example, for a considerable time, than is sulphur-cured rubber.

Accelerating Vulcanization with TNB

To accelerate vulcanization with TNB the following materials are required:

1. Metallic oxides and metallic sulphides (also compounds of metals with the elements of the oxygen groups O, S, Se, Te.). For example a mixture of 100 rubber, 150 zinc oxide, and 2 TNB is vulcanized perfectly in 25 minutes at 40 pounds' steam pressure.

2. Elements of the carbon group (carbon black, lampblack, amorphous carbon, graphite, silicon) as well as compounds of these elements with each other, for example carborundum (SiC). A similar action is shown by com-

Table II.—Vulcanization of Rubber with 1.3.5. Trinitrobenzene Without Sulphur, Activity of Special Accelerators

Experiment No.	1*	2*	3	4	5	6	7*	8	9	10	11*
Rubber, pale crepe	100	100	100	100	100	100	100	100	100	100	100
1.3.5. Trinitrobenzene	2	2	2	2	2	2	2	2	2	2	2
Aniline	1	0	1	1	1	1	1	1	1	1	1
Carbon black	...	...	10	100	...	...	100	...	...	...	...
Litharge	...	...	...	...	30	100	30	...	20	...	...
Zinc oxide (Kadox)	...	...	...	...	...	...	...	150	100	...	...
Chromic oxide	...	...	...	...	...	...	...	...	...	...	50
Magnesium oxide	...	...	...	...	...	...	...	...	...	175	...
Minutes at 141° C. for full cure.	No cure	No cure	90	30	30	5	5	20	15	5	60

*

1 and 2. In these stocks only the traces of vulcanization are noticeable in 180 minutes at 141° C. The product being like raw rubber, it can be easily milled, sticks together, and in time shows on its surface a delicate green deposit of a nitroso compound by Liebermann's reaction.

7. This stock also vulcanizes at room temperature.

11. This product is a beautiful green, possesses a good stretch and very low set. It is too weak and easily torn. It has a brilliant surface. In time it slowly develops tackiness.

Experiment No.	12*	13	14	15	16	17	18	19	20	21*	22*
Rubber, pale crepe	100	100	100	100	100	100	100	100	100	100	100
1.3.5. Trinitrobenzene	2	2	2	2	2	2	2	2	2	2	2
Aniline	1	1	1	0	0	1	1	1	1	1	1
Carborundum	...	...	...	...	...	...	...	...	...	180	100
Kieselguhr	...	...	...	...	...	100	60	...	...	...	...
Silicon	...	...	...	...	...	...	...	...	30	...	...
Litharge	...	...	...	...	...	...	10	30	30	...	...
Titanium dioxide	108	...	...	...	...	...	...	...	...	...	...
Calcium sulphide	...	...	...	...	100	...	...	...	...	...	...
Cadmium sulphide	...	...	75	75	...	...	...	...	...	...	...
Lead sulphide	...	60	...	...	...	...	...	...	...	...	...
Minutes at 141° C. for full cure.	No cure	25	180	15	30	90	5	5+	5	5+	60

*

12. This mix begins to cure in 105 minutes but its complete vulcanization requires 180 minutes. The cured product is somewhat tacky, weak, and easily deformed under mechanical treatment.

21. This stock overcures badly in 5 minutes. The product is a beautiful brown. A very brittle vulcanizate is produced in 30 minutes or more of heating at 141° C. The stock should be cured at about 125° C.

22 and 23. Upon prolonged keeping these vulcanizates show a greenish surface deposit. Hence it follows that acceleration of vulcanization by carborundum does not depend upon the amount of 1.3.5. trinitrobenzene used.

Experiment No.	23*	24*	25*	26	27	28*	29*	30*	31*	32*	32A*
Rubber, pale crepe	100	100	100	100	100	100	100	100	100	100	100
1.3.5. Trinitrobenzene	5	2	2	2	2	2	2	2	2	2	2
Aniline	1	1	1	1	1	1	1	0	0	1	1
Carborundum	100	...	...	...	...	100	50	...	...	100	130
Graphite	...	...	...	...	100	...	...	...	...	...	...
Talc	...	75	...	...	...	...	...	...	...	...	...
Aluminum powder	...	...	150	100	...	...	...	...	...	...	...
Ultramarine	...	...	...	...	...	...	...	75	...	...	...
Litharge	...	...	...	30	...	30	30	...	...	30	30
Boron, amorphous	...	...	...	...	...	...	...	...	100	...	...
Minutes at 141° C. for full cure.	60	180	105	5 to 10	45 to 60	5	5	105	90	5	5

*

24. Vulcanization is near completion in 90 minutes. The product is bright brown, somewhat resembling old leather. The set of the stock is very low and it can be torn with comparative ease.
25. This product is naturally leather-like.
28 and 29. Very good products. The carborundum must be used in very finely powdered condition.
30. This product is porous and on this account can be easily torn. Its surface is black but when cut it is clear blue.
31. When completely cured, this product appears to be hygroscopic. It is brownish red and smells disagreeably of phosphoric hydrides.
32 and 32A. Badly overcures in 10 minutes.

Experiment No.	33*	34	35*	36*	37	38*	39	40	41	42
Rubber, pale crepe	100	100	100	100	100	100	100	100	100	100
1.3.5. Trinitrobenzene	2	2	2	2	2	2	2	2	2	2
Aniline	1	1	...	0	0	0	...	1	0	0
Aluminum oxide	...	...	30	...	...	...	...	...	...	...
Talc	30	...	...	...	...	...	...	...	...	...
Silica	...	100	...	...	...	...	...	...	...	...
Kieselguhr	...	...	...	...	...	...	...	30	...	...
Litharge	30	...	30	...	...	...	30	30	...	30
Cadmium sulphide	...	...	...	70	140	70	...	...	...	...
Chromic oxide	...	...	...	...	...	...	30	...	100	50
Minutes at 141° C. for full cure.	10	90	10	No cure	No cure	110	5	5	160	5

*

33. Badly overcures in 25 minutes.
35. A very good product. In order to make clear the acceleration of vulcanization by aluminum oxide refer to Experiment 5 of Table II.
36. This shows no trace of vulcanization in 180 minutes at 141° C.
38. Shows no cure in 60 minutes. This mix without boron is completely cured in 30 minutes.

pounds, such as red phosphorus, powdered aluminum, talcum, ultramarine, mineral flour, etc.

The amorphous modifications of boron which, similar to amorphous carbon, readily absorb the different gases, do not accelerate vulcanization with TNB. Consequently, the action of this material, as contrasted with that of carbon, bears no relation to the gas-absorbing property of the latter.

An experiment specially conducted showed that carbon black, whether ordinary or saturated with air, accelerates vulcanization with TNB equally and to the same extent. From this we gather that in no instance do these accelerators serve as oxygen carriers.

Mixed Accelerators

The accelerators of the first and second groups named above apparently function differently from each other. A mixture of these accelerator groups always works more strongly than either of them by itself. See Table II. The total effect is always the sum of the separate effects. Evidently, the first group embraces the chemical and the second the physical accelerators. The action of these accelerators of vulcanization with TNB differs altogether from that of all known accelerators that have been used in vulcanization with sulphur. The effect, however, is alike in both cases. Certain compounds, for instance those containing kieselguhr or carbon black, carborundum, etc., while accelerating vulcanization, tend at the same time to improve the physical constants of the vulcanizate.

Speed of Vulcanization

Moreover, it has been found that the speed of vulcanization with TNB in the presence of zinc oxide depends largely upon the nature of the latter substance. Thus, a mixture of 100 rubber, 2 TNB, and 150 Kadox zinc oxide is completely vulcanized in 20 to 25 minutes, at 40 pounds, 141°C., whereas the same mixture, but with ordinary zinc oxide, requires under the same conditions 160 minutes, for complete vulcanization. Thus, vulcanization with TNB in the presence of Kadox zinc oxide takes place at a speed approximately six times greater than vulcanization with ordinary zinc oxide. Our observations show that Kadox in contradistinction to ordinary zinc oxide readily decolorizes aqueous solutions of methylene blue and of many other dyestuffs. Moreover, Kadox is distinguished from all other zinc oxides in that it contains a small amount of free zinc in the form of zinc dust, traces of germanium, etc.

Whether used with TNB or any other nitro compound, the accelerators of TNB vulcanization react on the whole in the same way. A mixture of, say 100 gms. of rubber, 3 gms. of meta-dinitrobenzene, and 150 gms. of zinc oxide will not vulcanize to any appreciable extent even though heated for two hours at 141° C. However, upon the addition of about

20 gms. of carbon black, the new mixture will vulcanize completely within 20 minutes. As a rule, meta-dinitrobenzene vulcanizes rubber much more slowly than TNB does.

Minimum Amount of TNB Required for Complete Vulcanization

The powerful accelerators in TNB vulcanization, as well as the accelerators in sulphur vulcanization, allow us to determine the exact minimum quantity of the vulcanizing agent required. By using a mixture of litharge and carbon black, we found that the minimum amount of TNB required for complete vulcanization of rubber lies between 0.25 and 0.5 per cent. For example, a mixture of 100 rubber, 0.25 TNB, and 30 litharge, plus 100 carbon black vulcanizes completely in 105 to 120 minutes at a pressure of 40 pounds, 141°C., whereas a mixture of 100 rubber, 0.5 TNB, and 30 lead oxide, plus 100 carbon black vulcanizes completely in 30 minutes under the same conditions. The latter mixture produces a leathery vulcanizate of the following average constants: tensile, 1,590; set, 0.12; and stretch, 3.1. Therefore it shows that 0.5 per cent. of TNB promotes complete vulcanization.

General Considerations

1. The time required for TNB vulcanization remains the same in the presence of organic peroxides (0.5 to 3.0 per cent.), whether TNB itself or any other nitro-compound is used.
2. The presence of sulphur (0.3 to 1.0 per cent.) or of ordinary accelerators (amine or amine plus carbon bisulphide) does not affect the speed of vulcanization with TNB.
3. If the amount of sulphur is increased (2 to 8 per cent.), or a large quantity of aliphatic or aromatic amines be used, the vulcanization process with nitro compounds will be retarded and the physical constants of the vulcanizate will be impaired.
4. Aromatic amines, sulphur, metallic sulphides, and especially antimony pentasulphide, some of the sulphur dyes, and tannic acid protect the TNB vulcanizates from oxidation and other chemical changes when stored in the open air. These substances should, however, be used only in certain and very minute quantities (0.3 to 1.0 per cent.).

Practical Use of TNB as a Vulcanizing Agent

The following stocks were vulcanized with TNB: stock for driving belts, for solid tires, a mixture of rubber and cement, and several leather-like vulcanizates. When tested, all these vulcanizates proved to be superior to those cured with sulphur.

Therefore we come to the conclusion that:

1. Belting vulcanized with TNB is twice as durable as belting made of a stock vulcanized with sulphur.

2. Leather-like products made of a mixture of rubber, TNB, and carbon black have a beautiful and glossy black coloring. They show no bloom and display higher tensile, while their set and stretch are but slight.

3. Solid tires vulcanized with TNB retain their homogeneity longer and show better resistance to wear than sulphur-vulcanized tires. They are also far more durable in use.

Tests of hardness, abrasion, and elasticity under pressure were performed in the laboratories under ordinary conditions. When compared with tests on rubbers cured with sulphur under the same conditions, showing the same constants and with the same general appearance, the TNB-cured products gave results which were not only equal to but practically in many cases much more valuable than those of sulphur-cured stocks.

Acknowledgment

The work described in this article was performed in the General Laboratories of the United States Rubber Co., New York, N. Y. I take this opportunity to acknowledge to Ernest Hopkinson and to A. E. Jury my appreciation for the interest which they invariably showed in the work and for the arrangements they made for conducting these researches.

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Temperature Coefficient of Vulcanization on a Litharge Compound

J. R. Sheppard

THE influence of temperature on vulcanization is too well known to require emphasis—it has been generally recognized for quite a number of years that the relation between temperature and time for ordinary curing ranges was logarithmic although there has been no unanimity as to the exact relationship. This doubtless is in part due to the varying experimental conditions employed by the investigators and possibly in some cases to less precise measurements. Table I, a partial bibliography, shows some values for the temperature coefficient which have been obtained and the conditions used. It will be seen that values ranging from 8 to 25 have been reported for the coefficient (in terms of degrees Fahrenheit required to double the rate of cure).

It is the purpose of this paper to recount the writer's determination of the temperature coefficient for a given litharge stock in press cures—it is not safe perhaps to infer from the present results what might hold under certain other conditions.

General

Rate of, degree of, and the temperature coefficient of vulcanization can be expressed only in terms of some property or properties of the stock assumed to be proportional to vulcanization; and indeed the term vulcanization in a given case takes its exact significance from the property assumed as its criterion. In the present instance the criteria are the several properties pertaining to the stress-strain curve, and free sulphur. While the final results showed no significant difference in the temperature coefficients for the several criteria, the latter, nevertheless, have been treated as separate functions so as to bring out any difference in their coefficients.

Figure 1A illustrates the kind of data sought and the treatment. In terms of the quantities actually measured, the temperature coefficient of vulcanization may be described as the relation between time (t) and temperature (T) which holds for all cures on a given stock resulting in a constant value of that property (P) taken as the criterion of vulcanization.

This relation is a case of the three-dimensional relation between the variables t, T, and P which shows the values of the property obtained at *all* times of cure and temperatures.

In outline, therefore, the procedure for determining the time-temperature relation characteristic of the temperature coefficient is (a) to carry out such variations of time and temperature, with observations on the corresponding values of the property, as are necessary to delineate the *general* time-temperature-property relation; (b) plot the general relation as a spacial locus; and (c) intersect the locus of the general relation with a constant property plane, the intersection being the locus of the temperature coefficient equation desired. In practice, in place of constructing a spacial graph, it is more convenient to employ the equivalent, namely a family of curves, as illustrated farther on.

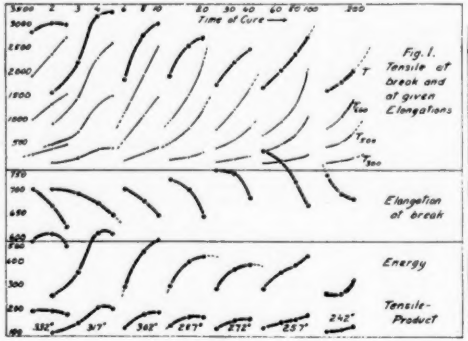

Fig. 1.

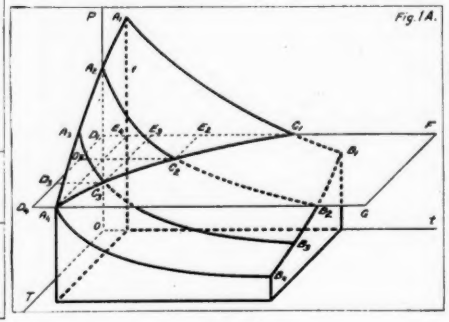

Fig. 1A.

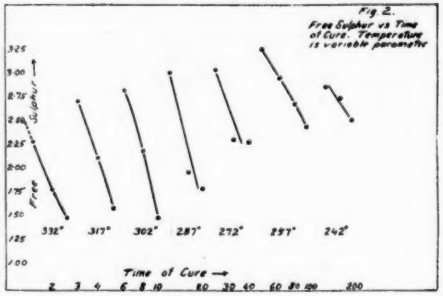

Fig. 2.

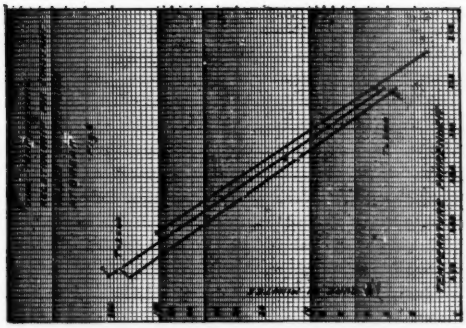

Fig. 6.

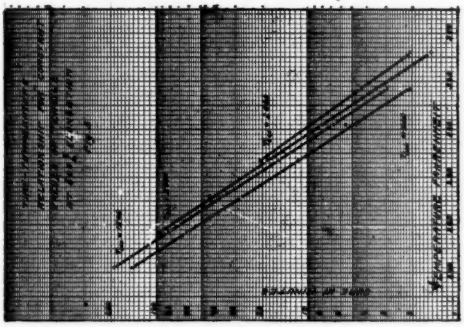

Fig. 5.

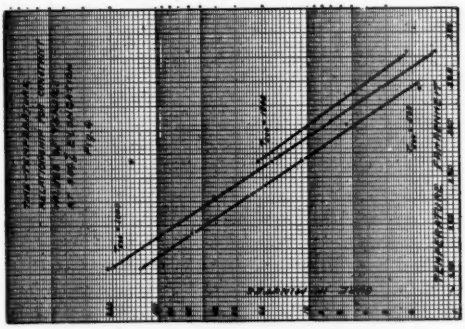

Fig. 4.

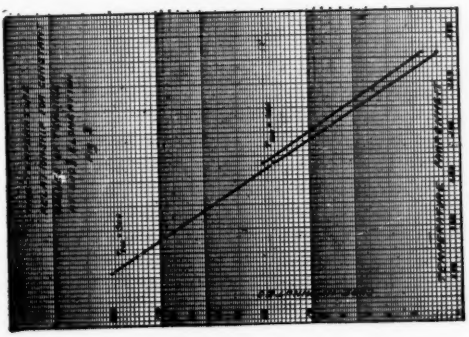

Fig. 3.

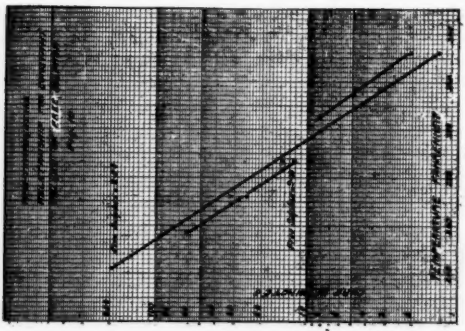

Fig. 10.

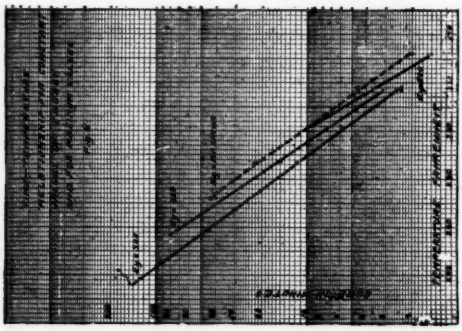

Fig. 9.

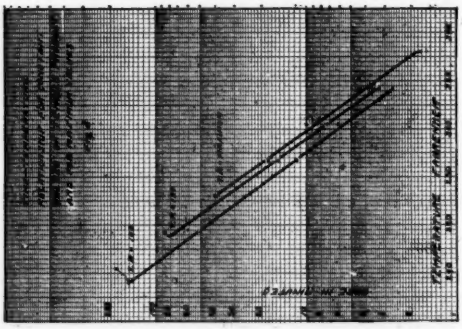

Fig. 8.

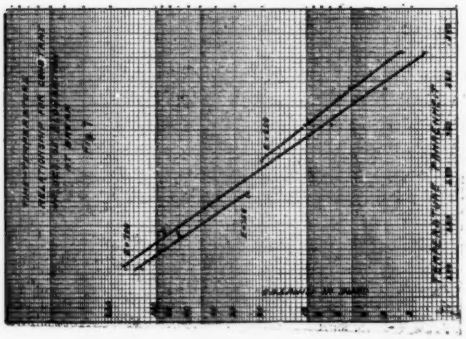

Fig. 7.

In Figure 1A the curved surface $A_1B_1B_4A_4$ is the locus of the property (P) as time (t) and temperature (T) are varied, (the general relation). We may presume this surface to have been determined by drawing it through the individual plane curves A_1B_1 . . . . A_4B_4 which are all in planes parallel to the POt coordinate plane, and we may presume that each of the latter curves has been determined through measurements of the property on a series of vulcanizates cured at constant temperature but for varying times. The curves A_1B_1, and so forth, are of course the "curing curves" of common practice, frequently involving tensile versus time. In the figure, the planes of the curves A_1B_1, A_2B_2 are spaced along the temperature axis OT so as to correspond with their respective temperatures. The plane D_1FGD_4 is parallel to the TOt coordinate plane and removed from it a distance OD_1, corresponding to the constant value of the property which it is desired to use as a criterion. The intersection of this plane with the general surface is in the line $C_1C_2C_3A_4$ and *this line is, with respect to the axes D_1D_4 and D_1F, the time-temperature locus for a fixed value of the property which is sought as an expression of the temperature coefficient of vulcanization.*

It is desirable, to increase the reliability of the result, to employ several planes parallel to D_1FGD_4 representing different constant values of the property, and, of course, in the case of a subject like rubber, where so many criteria of cure *can* be used, it is desirable to employ at least several criteria, if for no other reason, in order to establish whether or not the temperature coefficient is the same for all of them. There is no theoretical or *a priori* reason for presuming it is.

Experimental

It has not been attempted in the present study to cover a variety of compounds or types of vulcanization. On the contrary the work has been confined to press cures on a single litharge stock. A quantity of stock of the composition

Smoked sheet	100
Sulphur	8
Litharge	15
Zinc oxide	44
Stearic acid	1

was master-batched and press cures were commenced the next day, being continued over a period of 4 days. The temperatures of vulcanization ranged from 242°F to 332°F at 15-degree intervals and the times from 1½ minutes to 192 minutes, 3 or 4 different times being employed with each temperature. As in general the properties of a stock alter more rapidly in the early (undercure) part of a cure than in the later part, in the neighborhood of the optimum and in the overcure region, the properties during the early stages form a more sensitive criterion of state of cure than those in the more advanced stages. Consequently the times of cure for each temperature were chosen to yield in the main undercures, although as the data show the optimum was reached and passed in several cases.

In view of the short times involved at the higher temperatures it was necessary to minimize errors by due precautions. A mold maintained at the curing temperature between the platens for at least half an hour was withdrawn as quickly as possible, the single sheet of rubber which was to be cured was inserted, the mold returned and the platens closed on it. The time of cure was counted in all cases as commencing with the instant both platens formed contact with the mold and terminating with the instant that contact of the top platen with the mold was broken on release of the hydraulic pressure. The period between the termination of one cure and the commencement of the next at the same temperature, as defined above, was 1 minute or less. The mold had little opportunity to cool as during only a fraction of this period was it entirely out of the press.

The average gage of the cured sheets was .083″. The day following its cure, stress-strains were determined on each vulcanizate with the Scott machine by the two-observer method. Free sulphurs were also determined by the bromine

method[1]. These were done at somewhat irregular time intervals after vulcanization, within a period of about two months.

When planning the cures, it was assumed, in accordance with a quite generally accepted rule, that a rise of 15° F would entail a doubling of the rate of cure and this was the reason for making 15° the interval between consecutive temperatures. The choice of temperature and of time intervals in no way influences the relationship ultimately found, but is solely a matter of experimental convenience and more particularly of insuring that the zone of the time-temperature-property surface which will be delineated will be broad enough to include all or a goodly part of the intersection with the constant property plane.

Results

All results, namely stress-strain data and free sulphurs, are found in Table 2, which we need not comment on otherwise than to remark that it exhibits the well-known variations of properties with time of cure.

In Figure 1 all the physical data of Table 2 are graphed. Properties are plotted vertically and time horizontally, the latter to a logarithmic scale, well adapted to the purpose, as it enables both long and short cures to appear in the one graph, without crowding of the latter or undue spreading of the former. The data for a given property are plotted as a family of property-time curves with temperature as variable parameter, and as such can be made to function in the same way as the spacial locus of Figure 1A. The temperatures are noted near the bottom of the graph, associated with their respective groups of curves. In a number of cases extrapolations have been made, these being distinguished by broken lines.

The properties shown in Figure 1 as criteria of state of cure are: Breaking tensile (Marked "T"); Tensile at 600% elongation ("T_{600}"); Tensile at 500% elongation ("T_{500}"); Tensile at 300% elongation ("T_{300}"); Elongation at break; Energy; Tensile Product. Of these properties the greatest reliance is placed on the tensiles at given elongations because of (a) their sensitiveness to cure, and (b) the relatively high accuracy with which they can be determined.

Although Figure 1 is intended to serve only as the basis for building up Table 3, several characteristics are observable even on cursory examination and these may be noted. (a) Any two adjacent curves for a given property have about the same distance between them, measured along a given horizontal line (provided that, in the case of properties which reach a maximum, the measurement is not made too near the latter). (b) The several curves of a family are roughly of the same shape and orientation, so that the horizontal interval between adjacent curves is roughly the same irrespective of the level at which it is measured [with the same proviso as in (a)]. (c) The horizontal intervals between curves in one family and those in another are about equal. We need not comment here on the significance of these observations as this will be brought out in the more exact treatment of the data in the sequel.

In Figure 2 the free sulphurs are plotted similarly. Each line represents the free sulphur as the time of cure is varied; the temperature varies from line to line. The same characteristics regarding the spacing, shape, and orientation of the sulphur curves as noted above for the physical data are observable, although there is somewhat more experimental irregularity. For this reason, and because free rather than combined sulphurs are involved, less weight is, perhaps, to be attached in the present work to the chemical than to the physical results; notwithstanding which the former have yielded practically the same coefficient as the latter.

Figures 1 and 2 facilitate the derivation of the corresponding time-temperature values for constant properties. Table 3 shows the times and temperatures corresponding to from 2 to 4 fixed values of each property as read from Figures 1 and 2. Times derived from extrapolated parts of curves are shown in parenthesis in Table 3.

[1] "Standard Methods for the Analysis of Rubber Goods—Recommended by the Committee on Methods of Analysis of the Division of Rubber Chemistry of the A. C. S." *Ind. Eng. Chem.*, 16, 397 (1924).

Also in the case of tensile product and of energy the times for the various temperatures when the property reaches a maximum are shown.

In Figures 3 to 10, employing logarithmic time scales, the data of Table 3 are graphed, each figure displaying the time-temperature relationships for the several constant values of a given property. Points obtained by extrapolation in Figure 1 or 2 are denoted by a hollow circle.

TABLE I

Author and Conditions of Determination	Temperature Coefficient[1] I	II
A. O. Bourn[2] in 1905 on the formula F. Para 100, Sulphur 3, litharge 50, whiting 50, claims, in a short note lacking details, to have obtained "perfect" vulcanisations in 211 days at 105°F and in 1 second at 600°F. The method whereby the short cure was controlled is not indicated. He did not publish a temperature coefficient, but when such is calculated as a mean value for the above extremely wide temperature range we have ...	20-21	1.8
Spence & Young[3] in 1912 on rubber with 10% sulphur for the interval 135°C (275°F) to 155°C (311°F), using combined sulphur as criterion give	12.8	2.65
A. O. Bourn[4] in 1913 on the same formula as above subjected to dry heat cures found, for the interval 194°F to 252°F, on the basis of (unspecified) physical properties	11	3.1
The cures were continued up to 400°F, but at about 262°F the data indicate the commencement of a change in the coefficient such that a given temperature increment effects decreasing acceleration of the cure as the temperature rises. The extent of this lessening influence of temperature increase may be judged by citing the last interval viz. from 375°F to 400°F which shows	25	1.6
The 400°F cure is recorded as of 3 seconds duration.		
A. van Rossem[5] in 1918, using combined sulphur as criterion, found for the rather restricted interval 145°C (294°F) to 155°C (311°F)	18	2
Twiss & Brazier[6] in 1920 on the compound P. Crepe 90, Sulphur 10, for the interval 128°C (262°F) to 168°C (334°F) found using combined sulphur as criterion;	15.0	2.1
using extensibility at given elongation as criterion;	15.0	2.1
using time to reach maximum tensile as criterion;	14.2	2.4
Although they state that the coefficient "manifests no tendency to any regular increase or decrease with rise of temperature", a footnote indicates that "on account of the inconveniently rapid progress of vulcanisation at 168°C and its slowness at 128°C, the measurements at 138°C to 158°C are possibly to be preferred". The mean value obtained for this more limited interval on the basis of all three criteria was..	13.0	2.6
On the same formula as above with the addition of varying amounts of aldehyde ammonia ranging up to 1%, for the interval 108°C (226°F) to 148°C (298°F), on the basis of all three criteria the coefficient obtained was substantially as for the rubber-sulphur mix, namely	14.2	2.4
However, for the interval 98°C (208°F) to 108°C (226°F) a given temperature increment had markedly more effect namely	8	5
J. B. Sheppard in this paper, on the litharge stock detailed within, for the interval 242°F to 332°F, in press cures, and using as criteria various physical properties depending on the stress-strain and also free sulphurs finds as mean values	13.1	2.59
It is considered that no significant variation of coefficient is shown within this temperature range, and that no significant difference as between the individual criteria exists.		

Footnotes to Preceding Table

1. Column headed I gives number of degrees Fahrenheit required to double the rate of cure; column headed II gives the factor by which the rate is multiplied when the temperature is raised 10° Centigrade. The figure underlined was calculated by original author.
2. I. R. J., 33, 93 (1905)
3. K. Chem. Ind. Kolloide, 11, 28 (1912)
4. I. R. J., 45, 120 (1913)
5. Comm. of Neth. Govt. Inst. for Adv. Rubber Ind. Part VI, 179-222.
6. J. S. C. I., 39, 125T (1920).

Table 1. Partial Bibliography Showing Values for Some Temperature Coefficients Obtained and Conditions of Determination.

Figure 3 graphs the time against the temperature which results in the tensile at 300 per cent. elongation assuming the values 300 and 400 respectively. Two facts concerning the lines are pronounced: first that they are straight, corresponding with a logarithmic relationship; and second that they are nearly parallel. We may note in passing that, *granting straightness,* the parallelism is a mathematical necessity, since otherwise at their intersection we should have the absurdity of the same cure in time and temperature giving rise in the one stock to two different values for a given property. It follows that any lack of absolute parallelism found between the constant property lines of any one of these graphs is due to experimental error and is of no significance.

Figure 4 shows time versus temperature for constant values of tensile at 500 per cent. elongation, namely 500, 1,000, and 1,500; and Figure 5 similarly applies to tensile at 600 per cent. elongation fixed at 1,000, 1,500, 2,000, and 2,500. In these 2 graphs, as in Figure 3, we find quite good conformity of the determined points to the lines drawn through them, almost the only points seriously off the lines being certain of those got by extrapolation.

Figure 6 employs tensile at break and Figure 7 elongation at break as parameters. These, as also Figure 8 for tensile product and Figure 9 for energy, show, as might be expected due to the breaking-point error, a less perfect agreement between points and lines than the graphs for tensiles at given elongations. Nevertheless in no case is there any doubt as to the comparatively accurate placement of the line, nor is there in any case reason to believe that such deviations

Temp.	Time	Tensile at Elongation of							T	E	T.P.	Ey	% Free Sulphur
		100	200	300	400	500	600	700					
242	128	70	108	165	278	500	886	1455	1690	740	125	280	2.88
	160	77	128	198	331	591	1125	1845	1845	700	129	281	2.77
	192	87	150	262	431	805	1492		2092	690	144	341	2.53
257	48	62	89	152	215	416	734	1215	1735	790	137	300	3.28
	64	74	111	191	309	555	1015	1765	2110	770	162	374	2.98
	80	88	151	251	416	753	1387	2275	2437	725	173	398	2.71
	96	87	193	335	596	1130	2125		2812	677	190	342	2.47
272	24	74	98	159	282	479	864	1587	1797	750	134	300	3.07
	32	72	138	216	323	628	1287	2067	2285	743	169	386	2.33
	40	99	185	296	512	894	1715		2542	692	175	400	2.31
287	12	74	117	209	315	574	1040	1735	1992	730	145	313	3.03
	16	88	168	275	481	874	1590	2550	2625	708	185	413	1.99
	20	119	249	380	720	1302	2305		2797	652	183	437	1.82
302	6	84	121	206	352	642	1205	1900	1921	710	136	312	2.85
	8	102	179	357	635	1137	2006		2865	685	196	457	2.22
	10	138	287	470	827	1530	2605		3094	653	202	505	1.51
317	2	74	99	160	292	543	982	1600	1650	710	117	276	—
	3	81	157	254	447	803	1545	2275	2275	700	159	369	2.74
	4	106	260	449	780	1375	2375		3255	680	221	534	2.14
	5	151	293	476	837	1575	2690		3330	655	218	528	1.61
332	1.5	103	202	333	562	1070	1978	2845	2907	710	206	496	2.31
	2	127	275	439	792	1407	2442		3086	675	208	528	1.80
	2.5	144	318	520	872	1605	2800		3060	630	193	478	1.51

Table 2. Physical Properties and Free Sulphurs After Vulcanization for Various Times and at Various Temperatures.

as occur are of significance; there is nothing to warrant deviating from the straight in drawing the lines. In Figure 8 the maximum tensile product line takes on a general alignment parallel to that of the constant value loci. The same is true of the maximum energy line in Figure 9.

In Figure 10 the time-temperature relations for constant free sulphurs are shown. The data here show more experimental divergence than in most of the physical results. Nevertheless the general trend is clear and capable of fairly exact definition.

It only remains to deduce the coefficients from the time-temperature iso-property lines of Figures 3 to 10. The coefficient following from a given line depends only on its slope. In Table 4, the coefficients are summarized, the third column giving the figure deduced from each individual line. Such lack of identity as may be found among the coefficients for the several constant values of a given property implies an equal lack of parallelism among the iso-property lines and, therefore,

as explained previously, denotes experimental error. The proper treatment of these data, therefore, is to average the several coefficients for a given property. This is done in the last 3 columns of the table, the mean values themselves being found in the sixth column. The fourth column shows the number of points of determined data through which the iso-property line in question is drawn. As a 7-point line has more probability of accuracy than a 3-point line, the former should have more influence in deciding the mean. The product (in column 5) of the individual coefficient and the number of points by which it was determined has been taken as the weight to grant to a given individual coefficient and the total of these weights divided by the total number of points yields the mean as found in column 6.

TEMPERATURE °F		332	317	302	287	272	257	242
Time of Cure When Tensile at 300% Elongation Equals	300	(1.4)	3.15	7.20	17.5	40.0	90.0	(210.0)
	400	1.75	3.70	8.95	20.5	----	----	----
Time of Cure When Tensile at 500% Elongation Equals	500	--	(1.8)	(5.5)	(11.0)	25.0	59.0	130.0
	1000	1.43	3.35	7.4	17.5	(42.0)	91.0	(215.0)
	1500	2.2	4.55	9.8	(21.5)	----	----	----
Time of Cure When Tensile at 600% Elongation Equals	1000	--	2.05	(5.5)	(11.5)	26.5	63.0	145.0
	1500	—	2.95	6.7	15.5	36.3	83.0	194.0
	2000	1.52	3.5	8.0	18.6	(44.0)	95.0	----
	2500	2.08	4.30	9.5	(20.8)	----	----	----
Time of Cure When Tensile Equals	2000	--	2.65	6.1	12.0	26.7	59.5	182.0
	2500	--	3.2	6.95	14.6	38.7	82.0	(235.0)
	3000	1.65	3.6	8.8	----	----	(104.0)	----
Time of Cure When Elongation Equals	750	----	----	----	----	24.0	72.0	124.0
	700	1.65	3.00	6.9	17.0	39.0	88.0	160.0
	650	2.3	(5.1)	(10.3)	20.0	----	----	----
Time of Cure When T. P. Equals	140	----	2.65	6.1	(11.7)	25.0	50.0	185.0
	180	----	3.3	7.3	15.4	----	87.0	----
	Max.	1.75	4.4	10.0	18.0	40.0	----	----
Maximum Value of T.P.		215.0	228.0	202.0	187.0	175.0	>190.0	----
Time of Cure When Energy Equals	300	----	2.35	(5.9)	(11.7)	24.0	48.0	178.0
	400	----	3.15	6.9	14.8	40.0	80.0	----
	500	1.5	3.68	9.7	----	----	----	----
	Max.	2.0	4.5	----	(22.0)	(43.0)	----	----
Maximum Value of Ey.		528.0	540.0	----	(440.0)	(402.0)	>442.0	----
Time of Cure When Free Sulphur Equals	3.00	----	----	----	12.2	24.6	62.2	----
	2.50	(1.36)	3.36	7.2	14.5	32.4	93.5	197
	1.75	2.08	4.72	9.25	----	----	----	----

Table 3. Showing Times of Cure and Temperatures Corresponding to Fixed Values of the Several Properties. Data obtained from the intersections of horizontal (Constant Property) lines with the Property-Time Curves. Values in parentheses are from extrapolated intersections.

Observing the mean coefficients for the several criteria of vulcanization we find they range from 12.6 for tensile at 300 per cent. and tensile at 600 per cent. to 13.7 for tensile product, with a grand average for all criteria as listed in the table of 13.1. The mean coefficients do not disagree with the grand average sufficiently to warrant a belief that the divergence has significance. The extreme deviation, holding for tensile product, is 4.6 per cent. We should conclude that, within the limits of experimental error, all properties used have yielded the same temperature coefficient of vulcanization. There is no inference that the same conclusion applies to other conditions than here investigated, such as to other compositions or types of cure, or to more extreme temperatures.

However, as a matter of fact it is highly improbable that other compositions or higher temperatures would produce the same results.

The experimental results of this paper are fully expressed by the following equation:

$$\frac{t_1}{t_2} = \frac{I_2}{I_1} = 2^{\frac{T_2 - T_1}{13.1}}$$

or $\log t_1 - \log t_2 = \log I_2 - \log I_1 = .0230\ (T_2 - T_1)$, where t_1, I_1, T_1, and

Property	Value of Property	Degrees F. Halving or Doubling Time of Cure	Number of Reliable points on Curve	Product of Two Preceding Figures	Average No. of degrees F. Halving or Doubling Time of Cure.
Tensile	300	12.5	7	87.5	
at 300 %	400	12.8	4	51.2	
Elongation			11	138.7	12.6
Tensile	500	12.5	6	75.0	
at 500%	1000	12.5	7	87.5	
Elongation	1500	13.4	4	53.6	
			17	216.1	12.7
Tensile	1000	12.4	6	74.4	
at 600%	1500	12.5	6	75.0	
Elongation	2000	12.6	6	75.6	
	2500	13.3	4	53.2	
			22	278.2	12.6
Tensile	2000	13.4	5	67.0	
	2500	12.8	5	64.0	
	3000	12.6	4	50.4	
			14	181.4	13.0
Elongation	750	12.7	3	38.1	
	700	13.25	7	92.8	
	650	14.5	4	58.0	
			14	188.9	13.5
Tensile	140	13.9	5	69.5	
Product	180	13.5	4	54.0	
			9	123.5	13.7
	Maximum	13.4	5		13.4
Energy	300	13.9	5	69.5	
	400	12.9	5	64.5	
	500	11.5	3	34.5	
			13	168.5	13.0
	Maximum	13.6	4		13.6
Free	3.00%	12.9	3	38.7	
Sulphur %	2.50%	12.6	7	88.2	
	1.75%	14.0	3	42.0	
			13	168.9	13.0
				Average of above	13.1

Table 4. Showing the Temperature Increment Which Halves or Doubles the Time of Cure, Corresponding to Each Constant Property Line in the Time—Temperature Graphs, with the Average Increment for Each Property.

t_2, I_2, T_2 are respectively a first and a second set of values of time of cure, intensity of curing action, and temperature in degrees Fahrenheit.

More frequently perhaps the temperature coefficient of a reaction is expressed as the factor by which the rate is multiplied when the temperature is raised 10°C. So expressed, the temperature coefficient of vulcanization herein determined becomes 2.59, this number corresponding with the 13.1°F required to double the rate or intensity.

The original paper ended at this point, but in view of its importance the author has appended the following remarks on the extension of the method discussed.

Suggested Applications of the Method

It may not be amiss to point out how the present method can be applied to the more general study of vulcanization and of accelerators. While with litharge the temperature coefficient appears, within ordinary curing ranges, to be representable by a constant, doubtless there are cases where, on the contrary, a variable depending on temperature is involved. In any event, whether constant or variable, the coefficient, when graphed as a time-temperature locus, expresses the vulcanizing propensity of a stock under changes of temperature.

Figure 11 represents some hypothetical cases which illustrate how curing properties are reflected in the coefficient lines. A is a stock with a constant

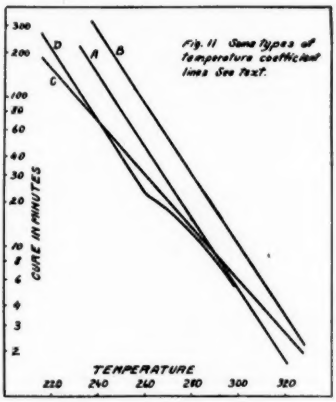

Fig. 11.

temperature coefficient, here made equal to 13°F. B is another stock which, although its temperature coefficient is identical with that for A, at all temperatures, takes twice as long to cure as A. On the other hand C cures equally with A at 290° but at 240° it is seen to cure in half the time for A. Therefore, as compared with A, C is specially quick curing at low temperatures; or A is relatively fast curing at high temperatures compared with C. If A, B, and C owe their different curing characteristics to their being compounded with different accelerators, it is obvious that, relatively, accelerator A is more powerful or active than accelerator B; on the other hand C cannot be described as more active than A—it is more correct to describe C as being (compared with A) a "low temperature" accelerator. The delineation of curing properties as a function of temperature in this way distinguishes neatly, therefore, between "low temperature" accelerators and rapid or powerful ones.

A low temperature accelerator may possess its special characteristics because of its stability below and instability above some (critical) temperature. If the loss of curing agent be abruptly dependent on temperature, rather than a gradual function thereof, then in the neighborhood of the temperature above which the loss occurs we should expect a sudden break or discontinuity in the coefficient line. This is illustrated by D where a sudden change occurs at about 260°; so that while below this temperature we have a stock curing in half the time for A, above we have an approach to the curing activity of A. A sudden change in the direction of the coefficient line is evidence of a change at the temperature in question in the character of the curing agents or in the mechanism of vulcanization.

It is suggested that a more extended study of temperature coefficients might throw light on such problems as: the more exact evaluation of the fitness of an accelerator for low or high temperature cures; the comparative effects of various types of cure such as mold, dry heat, live steam, and so forth; instability and volatility of accelerators or their products; the coupling of accelerators to avoid scorching, as in the use of litharge to prevent scorching with thiuram disulphides; comparisons of different activators with a given accelerator; adsorption of accelerators by reenforcing agents; and other of the numerous problems having to do with vulcanization as related to temperature, type of cure, and composition of stock.

Acknowledgments

The writer wishes to acknowledge his indebtedness to J. S. Blakeney and to J. F. Weiler for assistance in the accumulation of data and in the preparation of the graphs that have been used in this paper.

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The Value of Reclaimed Rubber in Tread Stock

C. W. Sanderson

VOGT[1] has published work showing that reclaim hydrocarbon has a value, judged by laboratory abrasion resistance in tread stock, varying from zero when used in small quantities up to a maximum of 50 per cent. of the value of new rubber when compounded in large percentages. This work was followed up by Gagnon,[2] who worked with stocks in a range between the base stock and Vogt's first reclaim compound, and he showed a high negative value for small amounts of reclaim. He also showed that the effects of adding reclaim depended on the base stock. If the abrasion of the base stock has already been lessened by diluents, the substitution of reclaim has relatively less effect than substitution of reclaim in a high grade stock.

In the work mentioned so far due allowance had been made for the mineral ingredients of the reclaim and all comparative compounds were on an equal ultimate composition basis. Gagnon in further work used a different method when he took a non-reclaim tread and a high reclaim tread and blended them in definite proportions to get intermediate stocks. He concluded that judged by abrasion resistance the value of the reclaim hydrocarbon is negative, becoming positive at about 40 per cent. reclaim hydrocarbon and having a value of 50 per cent. of new rubber in an all reclaim stock.

In none of this work was there any opportunity to check the compounds in service. The present work, therefore, was undertaken with this object particularly in mind. Advantage was also taken of the opportunity to compare physical properties, in addition to abrasion resistance, with service and thus make a study of the value of these properties in evaluating compounds for road wear.

[1] *J. Ind. Eng. Chem.*, Vol. 20, p. 140, Feb., 1928.
[2] Unpublished work, The Goodyear Tire & Rubber Co.

Experimental Reclaim Used

The reclaim used was a typical high-grade whole-tire alkali-process reclaim. Its composition was as follows:

Acetone extract	8.84
Chloroform extract	22.00
Free sulphur	0.09
Total sulphur	2.54
Carbon black	10.00
Ash	21.11
Sp. Gr.	1.15

When cured with 5 per cent. sulphur for 18 min. at 40 lbs. (141.5° C.), it gave a tensile of 55 kg. per sq. cm. and an elongation of 430 per cent. The hydrocarbon content of the reclaim was figured at 55 per cent.

Method of Compounding

In this work we took a high grade tread and an all reclaim stock and obtained three intermediate stocks by blending. The all reclaim stock was compounded to give maximum abrasion resistance consistent with ability to handle in the factory.

TABLE 1

	1	2	3	4	5
Rubber	100	75	50	25	0
Whole tire reclaim	0	45.5	91	136.50	182
Zinc oxide	6	4.5	3	1.50	0
Carbon black	43	39.55	36.10	32.65	29.20
Pine tar	6	4.5	3.0	1.5	0
Stearic acid	3	2.8	2.59	2.39	2.18
Sulphur	3	3.23	3.46	3.69	3.92
Captax	1	0.87	0.73	0.59	0.45
	162.2	175.95	189.88	203.82	217.75
Sp. Gr.	1.12	1.15	1.18	1.20	1.23

Since these are all on the basis of 100 rubber (figuring the reclaim 55 per cent. reclaim hydrocarbon), the proportions are obvious. The carbon black is lowest in the all reclaim stock but if we figure in the black of the reclaim the loading goes up with the series.

There are two rather obvious criticisms of this series. The first is that more stocks might have been taken particularly between zero and 25 per cent. reclaim hydrocarbon. The second is that in this method we have not allowed for the activating effect of the reclaim. The middle stocks, particularly No. 2 and No. 3, are relatively faster curing. It was felt that it was better to do this and let the cure vary rather than adjust the accelerator. The physical tests were all done over a range of cure, and it was not considered necessary for the road test as other work had shown that road wear (at least within reasonable age limits) is not sensitive to cure variations.

The procedure followed was to put up a quantity of No. 1 and No. 5; then No. 2, No. 3, and No. 4 were made up of blends of these two in the proper proportions. The black was used as a 60-40 master batch with the rubber and

as a 75-25 master batch with the reclaim. The latter was refined before using.

Road Tests

TAXICAB. The stocks were run as two-way treads on 30 by 5. The comparisons were No. 1 vs. No. 2, No. 2 vs. No. 3, No. 3 vs. No. 4, No. 4 vs. No. 5, No. 1 vs. No. 3, and No. 1 vs. No. 5. There were sixteen tires in each lot. The test was run on taxicabs in Philadelphia and covered a period from August 1 to November. The tires were applied to front or rear as needed, but the tests represent mostly rear mileage. The wear was obtained by button height and over all thickness measurements.

TEST CARS. The same comparisons with two tires in each set were made on 4.50/21 and run on a Dodge test car, rears only. The tires were rotated every 700 miles. The tires were measured when the faster wearing half showed approximately two-thirds of the button height loss. This test was run the last week in August.

Physical Tests

All physical tests were made on factory mixed stock. The sample was taken from the tubing machine at the time of running the treads for the test tires. Standard procedures for physical testing were used except as herein noted.

ABRASION. For convenience we have referred to Vogt's paper in designating the abrasion methods.

Method A—Regular Goodyear machine, 16° angle.
Method C—30 per cent slip.
Method D—20° angle.
Method E—Grasselli abrader.

WHEEL ABRASION. For this test a 30 by 5, one-way tread was run on a dynamometer with the wheel covered with sandpaper and under the following conditions: Load 750 lbs., inflation 30 lb./sq. in., speed 25 m.p.h., traction 375 lbs.

TEAR TESTS. This was not intended to be an exhaustive comparison of tear methods but several are included as this work did offer an opportunity to compare results on an evaluated series of stocks. There is no attempt to make out a case for any particular method. We do feel, however, that it is practically impossible to get values from any method which attempts to take into account the knots of carbon-black stock. The knotting is undoubtedly an important characteristic of the stock but the actual values obtained when they develop are meaningless.

GRAIN TEAR. This method is an attempt to get a numerical value for the hand-tear test. The test piece, 2 mm. thick, is cut and torn in the test machine and values are read from those places where the stock tears with the grain and does not knot.

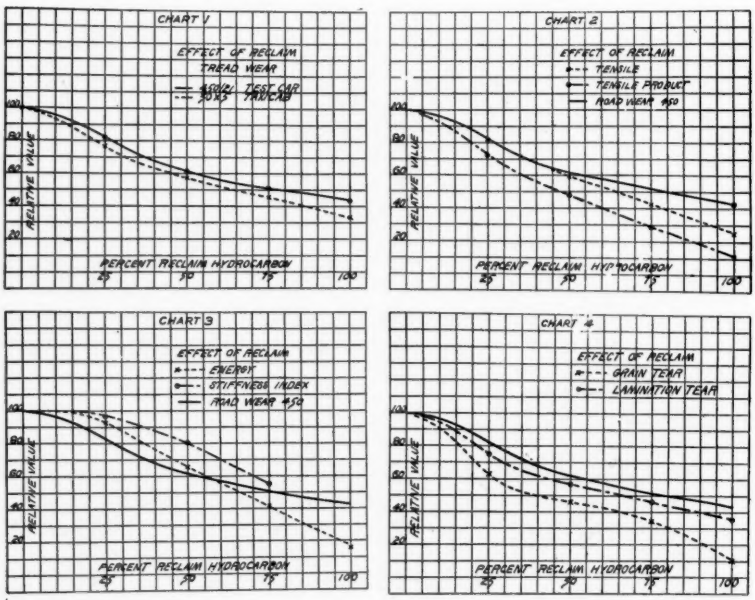
LAMINATION. The test piece, 4 mm. thick, is cut to tear

with the laminations, i.e., in a plane parallel to the mold surface. The pull required to tear a specimen 1 cm. wide is recorded.

SHEAR. This test was made in a special apparatus in which a 2 mm. sheet is held and a plunger pushed through it. The apparatus is designed so that a minimum of flow and distortion takes place. The plunger cuts through the sheet with a shearing action and the force required is measured.

REBOUND OR MECHANICAL EFFICIENCY. This test is made by the pendulum method.

FATIGUE. A strip of rubber 1 cm. wide was suspended from an upper jaw, while from a lower jaw was hung a



weight sufficient to cause an elongation of 250 per cent. The upper jaw moved through a three-inch stroke 350 times per minute and the test consisted of subjecting the specimen to this action for five minutes. The stress-strain curve of the stock was taken after the test and compared to a similar curve for an original specimen.

Results of Road Tests

The results of the road tests are shown as relative values on Chart 1. The test-car test gave exceptionally good checks from tire to tire and in the cross comparisons. The agreement between the test-car run and the taxicab test is closer than we anticipated.

Tensile Properties

The tensile properties at best cure are shown in Table 2.

TABLE 2

Stock No.	Time of Best Cure at 258° C.	Tens.	Elong.	Load at 300%	Load at 500%	Tens. Prod.	S. I.*	Energy Kg.cm./cm.³
1	70	300	690	62	166	207	104	670
2	50	250	590	94	194	147	100	612
3	50	184	550	82	166	100	84	440
4	60	122	490	68	(124)	60	56	257
5	60	76	380	56	...	29	..	111

*S. I. = Stiffness Index = Difference in load between 500% and 300%.

The relative values for tensile and tensile products are shown on Chart 2. On each chart we have shown for comparison the test-car treadwear curve. The tensile follows the road curve fairly well while the tensile product does not show so good a comparison.

Energy of resilience and stiffness index, both of which are used as criteria for the evaluation of tread stocks, are shown on Chart 3. Neither correspond to the road values so closely as does the tensile.

Tear

The relative values for tear are given on Chart 4. The lamination tear results give a fairly close indication of the road wear.

Abrasion

The abrasion-machine results on Chart 5 show that the best indication is given by C, the 30 per cent. slip method, and by D, 20° angle method. The Goodyear machine, A, and the Grasselli abrader are quite close together.

Mechanical efficiency, hardness, and shear are shown on Chart 6. The mechanical efficiency stays up better than any other mechanical property. It is practically constant from 25 per cent. reclaim hydrocarbon on as is likewise the hardness. The shear coincides with road value down to 50 per cent. and then falls off more rapidly.

Fatigue

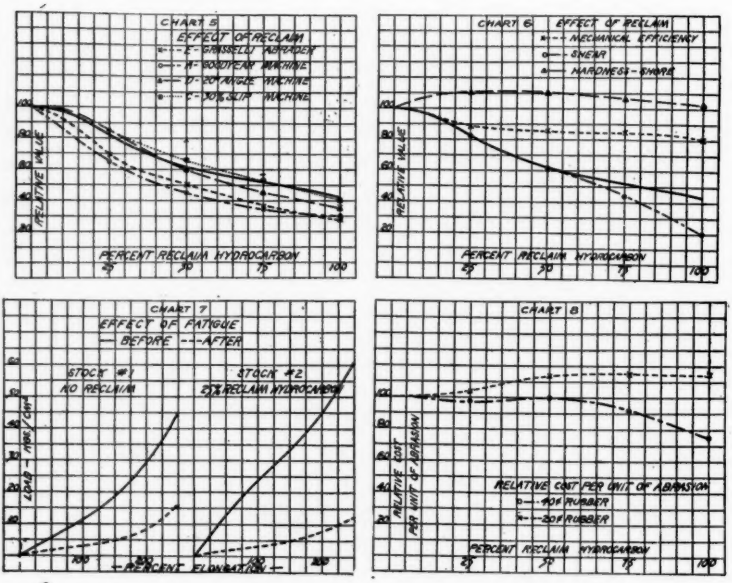
The conditions chosen for this test were so severe that only the No. 1 and No. 2 stocks stood the test without breaking. Curves are shown for the best cures on Chart 7. It will be noted that the apparent stiffness of the No. 2 disappears on this test. The energy at 250 per cent. elongation may or may not be significant but the following figures are of interest.

	Stock No. 1 Kg. cm./cm.³	Stock No. 2 Kg. cm./cm.³
Energy before fatigue	44	68
Energy after fatigue	13	13.2

Discussion of Results

In interpreting these results, we must keep in mind that they are based on one type of compounding variation. Because a certain property follows the road curve quite closely, it does not follow that this property would give the same indication of service on another type of compounding. Sweeping generalizations cannot be drawn and we emphasize this point in order that unjustified conclusions may not be drawn. In looking over the charts we see that tensile and lamination tear are the two most indicative tests.

Of the abrasion tests the 30 per cent. slip and the 20° angle methods seem best. The Grasselli and the Good-



year machines do, however, give results parallel after the 25 per cent. point so that comparison between two stocks in this range would give relative values corresponding to the road.

The shear test follows exactly down to 50 per cent. reclaim hydrocarbon and then falls below the road abrasion curve. By referring back to Chart 2 it will be seen that the shear is very close to the tensile. That seems to be the general indication with this test. This may either mean that shear and tensile really go together or it may be that this only follows because of the way in which we conduct the test. At any rate this is of interest in connection with the speculations on the role of cutting and tearing on abrasion.

Unfortunately our fatigue test as applied was of little use. It does show, however, that the stress-strain properties change very decidedly after the rubber is subjected to working action. From the fact that stock No. 1 will stand the action of the test for days, while stocks Nos. 3, 4, and 5 will stand it only a few seconds, we see that we have here one property on which the reclaim has a very marked effect. The relatively good showing of the reclaim stocks on the mechanical efficiency test is subject to a good deal of question in view of the fatigue test.

We find very little in these results to encourage efforts to evolve evaluation formulae. In the first place tensile and tear by themselves seem to be closely indicative and in the second place the fatigue test gives us reason to believe that the properties of the unstressed stock are of fictitious value. Coming down to the question of evaluating the reclaim hydrocarbon, we see from the road abrasion curve that it has a positive value at all points.

Using the method as given by Vogt where:

A=value of abrasion resistance of new rubber hydrocarbon, and let it be assigned a value of 100 units.

B=value of reclaim hydrocarbon in the same units.

C=experimentally determined values for abrasion resistance.

Y=amount of new rubber hydrocarbon as a decimal fraction and 1.00—Y—amount of reclaim hydrocarbon as a decimal fraction.

Then $AY+B(1.00—Y)=C$ on the assumption that the qualities of the two types of hydrocarbons are additive.

Solving

$$B = \frac{C—AY}{1.00—Y}$$

Using this on the road values we have:

TABLE 3

Value of Reclaim Hydrocarbon

New Rubber Hydrocarbon Per Cent.	Reclaim Hydrocarbon Per Cent.	B Values from Road Test
100	0	..
75	25	32
50	50	25
25	75	34
0	100	42

B is not worked out for the laboratory determined properties because the relation is perfectly clear from the charts.

The real evaluation of the reclaim should be on a cost basis. We have done this in the following table and have shown the relative cost per unit of abrasion on Chart 8.

In order to show the wear on an equivalent cost basis we have shown the relative cost per unit of abrasion. Taking No. 1 stock as the standard, we have obtained the cost of an amount of stock to give the same wear and then shown this

TABLE 4

Cost per Unit of Abrasion

Compound No.	Per Cent. Reclaim	Road Value	Sp. Gr.	20-Cent Rubber 7-Cent Reclaim Lb. Cost	Vol. Cost	Unit Abr. (Rel)	40-Cent Rubber 8-Cent Reclaim Lb. Cost	Vol. Cost	Unit Abr. (Rel)
1	0	100	1.12	.1497	.1677	(100)	.2757	.31	....
2	25	82.5	1.148	.1241	.1425	(104)	.2159	.25	(98)
3	50	62	1.175	.1022	.120	(115)	.1651	.193	(100)
4	75	51	1.20	.0835	.100	(117)	.1213	.145	(92)
5	100	43.5	1.23	.0671	.084	(115)	.0832	.102	(76)

as a relative figure in the column headed "Unit Abr. (Rel)." The cost per unit of abrasion is obtained by dividing the volume cost by the relative abrasion value.

On this basis at 20-cent rubber the reclaim is uneconomic at all points. It rises to a relative value of 115 at 50 per cent. and then stays constant. At 40-cent rubber the relative value stays about constant until 50 per cent. when it drops and at all reclaim it gives about 25 per cent. more for the money. In the above consideration we have neglected that fact that abrasion value is not the only factor to be considered. In many cases a certain volume or body is required and the use of reclaim compounds is justified.

Summary

The road abrasion value has been determined on a series of tread stocks containing from 0 to 100 per cent. reclaim hydrocarbon. There is a close check between the road value as determined on two different types of road tests. The value of reclaim in this test is shown to vary from .25 to 42 per cent. of the value of new rubber, being higher for the all reclaim stock. The relative cost per unit of abrasion is shown to be above rubber at all points for 20-cent rubber. For 40-cent rubber it is lower than rubber when used above 50 per cent. reclaim hydrocarbon. The relative values for laboratory tests are compared to the road value. The tensible, lamination tear, and the 30 per cent. slip abrasion seem to give the best indication of road value.

Acknowledgment

The writer wishes to express his appreciation to W. W. Vogt for valuable suggestions and criticism and to George Albertoni who performed most of the physical tests and who developed the shear and fatigue tests that are recorded in this paper.

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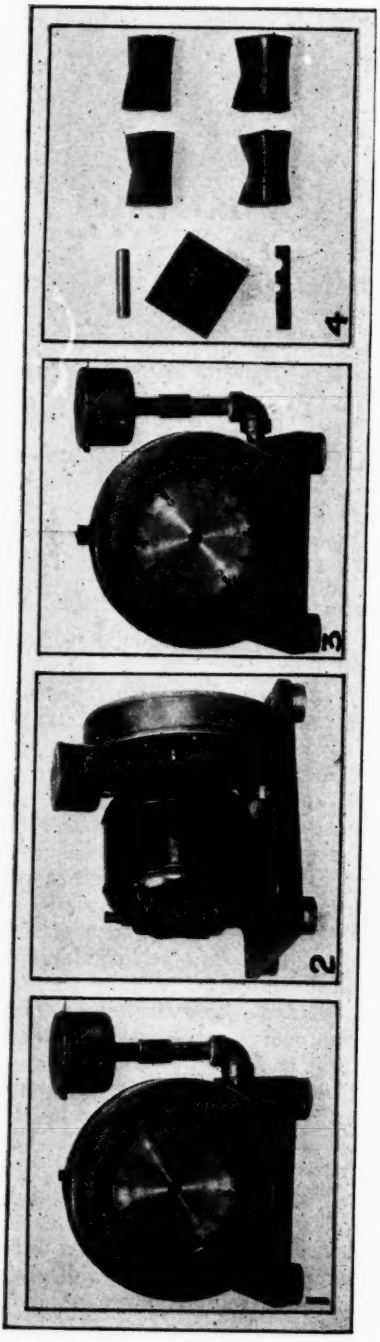
A New Flexing Machine for Rubber

Philip M. Torrance and Lester C. Peterson

TREAD cracking is one of the most annoying problems occupying the attention of rubber chemists at the present time. While there is no doubt that tread design and the construction of the tire as a whole have great influence in producing this phenomenon, the nature of the tread compound itself is a very important factor. A real need has been felt in the industry for a laboratory flexing machine which would rapidly and inexpensively give results comparable to those obtained in road tests in order to study the effect that variations in compounding have upon this type of failure.

The authors have developed a simple machine which it was felt might be of interest in this connection. Illustrations 1 and 2 are front and side-view photographs of this machine. It consists of a rotor disk one inch thick keyed to the shaft of a ¼ h.p. induction motor and radially slotted about its periphery to take twelve samples. Around this is a steel ring placed off center in relation to the rotor. The test samples are mold-cured slabs of rubber 1 inch wide, 1⅛ inches long, and 3/16-inch thick, having two semi-circular grooves molded across their width. When placed in a slot of the rotor, a test piece is held in place by a tightly-fitting cylindrical steel pin which fits in one of the semi-circular grooves in the test piece and in a similar groove cut in the wall of the slot.

Illustration 3 is a photograph of the machine with twelve samples in place ready to run. It will be noticed that as the rotor turns, the test pieces are flexed through a 90° angle as they pass that point on the ring closest to the rotor and are straightened out again at the opposite side of the ring, not only by their own elasticity but also by centrifugal force. The second groove in the test piece is located on the inside of the bend and serves to localize the flexing action. Since the motor operates at a speed of approximately 1,725 r.p.m., considerable friction would be developed were it not for the fact that the samples are lubricated with glycerine, which is fed into the machine through a small hole in the flexing ring by a wick-feed lubricator noticeable to the right of the


4
3
2
1

ring in the illustrations. The glycerine is kept from flowing out of the ring by retaining rings somewhat smaller in internal diameter located on either side of it.

Illustration 4 is a photograph of some test pieces. There are two views of an unflexed sample together with a locking pin as well as four bent pieces that have been flexed for 24 hours or approximately 2,484,000 times. The two that are cracked nearly through are duplicates of a stock accelerated with an aldehyde-amine type accelerator and containing no antioxidant. This stock was repeatedly shown to crack badly when run on a test car. The two uncracked samples, run on the machines at the same time as the others, are duplicates of the same compound after 1¼ per cent. of antioxidant has been added. It will be noticed that cracking has barely started, there being several pin-holes in the surface of each. This stock when run on a car showed no signs of cracking.

In general, the results of this machine check qualitatively with the road tests run to date. The results obtained so far indicate that certain antioxidants are of value in checking tread cracking and others are valueless. Modulus and methods of processing apparently exert an influence on this phenomenon.

Particular care must be taken when using mill-sheeted stock for test pieces, for it has been found that "cold checks" and pronounced grain effects cause premature cracking, a phenomenon probably related to the premature cracking at the junction of the tread and sidewall of a tire.

By means of a thermometer inserted in a mercury well in the top of the flexing ring, shown in illustration 3, considerable variations in operating temperature were observed. Because of this it has been decided to mount the machine in a constant-temperature water bath before further work is done.

It is expected that the following advantages will result from this modification: that the machine will be able to run under identical conditions; that there will be an opportunity to study the effect of different temperatures through a wide range; and that lubricating samples will be simplified.

The authors wish to express their appreciation to the India Tire & Rubber Co. for permission to publish this paper, and to Olin C. Work for suggesting the simple holding device for the samples.

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Electric Motor Drives *for* Rubber Machinery

R. D. Crawford

THE B. F. Goodrich Co. began in 1898 to use electric motors experimentally to drive calenders. Since that time there has been a steady addition of motor drives and a marked increase in all the equipment required to meet the additional electric power demand. In 1910-11 certain gear driven calenders were changed over to motor drive. The gear drives on calenders made available only two speeds by means of gear changes. The maximum yardage rate was 18 or 19 yards per minute and the minimum, about half that speed with no possibility of an intermediate speed. It is now possible to make almost any adjustment desired, while speeds have been increased greatly, even up to 50 yards or more per minute.

With respect to a calender, heating naturally increases as the friction ratio increases. Thus the stock becomes hotter at higher rates of production necessitating installation of better cooling facilities. For example, changing the friction ratio of a certain calender from 1½ to 1 to 2 to 1, delivery of the same yardage rate was impossible until the calender piping of increased size was rearranged to permit the circulation of an increased volume of water. This increase of friction ratio demanded more power from the motor. It has been found a good rule of thumb that the proportionate increase of power is about equal to the sum of the peripheral speed of the rolls either of calenders or mills.

The electric drive has been the means to study the peculiarities of the power demands for individual rubber manufacturing processes and to estimate the mechanical strains in machines, thus enabling the designer to make proper allowances for the factor of safety in gears and other parts. The portable graphic wattmeter is very useful for securing data to use in designing a drive to meet specific conditions of power and strength.

As early as 1909 or 1910 the size of motor to drive a line of 84-inch mixing mills was fairly well established but not so with respect to crackers, sheeters, single warming mills, etc. With respect to this group the power problem was

solved by making ample allowance in the power-supply circuits and in the pull-out torque of the motor.

Synchronous motors were applied for rubber work in 1919. The advantage of this type of motor was considered to be power-factor correction and somewhat higher pull-out torque obtainable when occasion required. The same problem of safety was present with synchronous as with induction motor applications, that is, the magnetic clutch had to be retained because of the very low starting torque of the synchronous motor that was first offered as rubber mill drives. Improved synchronous motors are practically all that can be desired from the standpoint of assured starting ability, pull-out torque, and safety. The emergency stop can now be secured by means of dynamic braking or plugging. The magnetic clutch served well in its day but the synchronous motor is much more satisfactory as to safety and other practical features.

It is virtually settled that for most lines of 84-inch mixing mills there should be an allowance of about 125 h.p. per mill to carry the peak loads. In certain classes of work, however, larger motors are needed and again the motor rating can be reduced. In the operation of rubber crackers the ratio of average load to peak load is usually 3¼ or 3½ to 1. The average load of a cracker is not much over 50 or 60 h.p., while the peak may reach momentarily as high as 200 h.p. or practically 4 to 1. The ratio of average load to peak load in the case of a sheeter is about 1½ to 1.

The Banbury mixer is the most recent development in rubber mixing machinery. Originally there was much discussion as to its proper size of motor. The present practice is to use a unit coupled direct to the line shaft and having a rating of 500 h.p. for size No. 27.

For the operation of a 16 by 42-inch warming mill it seems definitely settled that a 75 h.p. induction motor is sufficient for all classes of work and a 150 h.p. motor for a 20 by 60-inch mill. The synchronous motor is considered the best drive for a single mill when taking into account just the factors of pull-out torque and power-factor correction. If the latter point is not essential and first cost is important, an induction motor is used provided pull-out torque is sufficient.

In making application of synchronous motors to individual warming mills the 125 h.p. .8 P.F. motor does very well for the 20 by 60-inch mill. In the case of the 16 by 42-inch mill the 75 h.p. .8 P.F. motor may as well be chosen since the 60 h.p. size does not cost much less. There is the further consideration that the single mill installation is often on feeder with many small motors. In such case the surplus capacity above that required for the mechanical load can well be employed for power-factor correction.

Tubing machines are about the most troublesome of any to which to apply motors, especially in a department

where miscellaneous work is conducted with frequent changes in stocks and die sizes. About the only way to cope with such a situation is to apply a motor large enough for the extreme condition and risk so that it will be run below its rating more or less of the time. It is pretty well settled that a 6-inch tubing machine with worm speed of 65 r.p.m. operating on tire tread or tubing requires a 50 h.p. motor. There can be variations from these specifications to comply with special power requirements.

The use of conveyers is entering into many manufacturing methods. They are freakish things to which to apply motors because of the excessive starting effort they require compared with their average load value after the motor has brought them to full speed. In general the torque required to start is 2.3 times the running torque of the load as found. The choice of motor then is the one nearest to that value. This rule applies more especially to belts dragging on stationary supports. Where the belt is supported by rollers mounted in ball-bearings, the starting effort is much less. At best the job is always over-motored and this will continue so until a motor is produced that will have much better starting ability and yet have good efficiency and power factors. The realization of this may be a long way off; so the best expedient in nearly all cases is the standard squirrel-cage motor.

In many rubber plants where there is occasion to use motors, they probably do not run above 10-15 h.p. and the large majority 7½ h.p. and below. In the case of motors of 10 h.p. and over it should be possible to find motors having special starting torque characteristics, which would considerably simplify the problems of motor applications in the larger installations.

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Some Practical Methods of Measuring Gauge at the Calenders*

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The B. F. Goodrich Company

A LITTLE reflection will immediately establish the fact that it is necessary to control, in some manner, the thickness of practically every stock delivered by a calender, and that this control is indicated by the twin considerations of quality and cost. As an illustration, consider coated fabrics used for tire carcass construction. From the standpoint of quality the skim coat applied to the fabric during calendering must be of sufficient thickness to insure adequate insulation between the plies in the completed tire. Not only must the average thickness be more than a certain minimum but it must be uniform, for non-uniformity results in heavy gauge in some regions and light gauge in others, the latter being a fruitful source of failure by ply separation in service, on account of excessive stresses developed by loading and traction. On the other hand, a skim coat which is too heavy may actually lead to deterioration in quality by introducing defects caused by increased difficulty in tire building. Another example that may be cited is the tread slab, tubed or calendered. Light gauge here may result in incomplete filling of the mold, producing blemished tires; on the other hand, a tread slab that is too heavy may cause a more serious defect, buckled carcass, due to excessive rind at the mold register. In the case of solid tires, correct gauges are of utmost importance. And so one may instance an almost endless number of examples of the necessity of preserving quality by controlling gauge—in footwear,

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belting, hose and other mechanical products, rubber sheet for thread of all kinds, hard rubber compounds for panels, battery jars, etc.

On the side of production cost, excess gauge (beyond the requirements) may result in enormous losses. To illustrate: Let us consider a calender delivering material 54 inches wide at an average rate of 25 yards per minute for 24 hours, 300 days a year. (This is a conservative example for a calender in continuous operation in a large plant.) The annual output of this machine would be 16,200,000 square yards. Now, if carelessly or intentionally, the average gauge of this were only .001 inch greater than specified, the excess gum required would amount to 12,150 cubic feet, or, at a gravity of 1.0, about 760,000 pounds. If the material cost be taken at 50 cents per pound, then the loss in a single year would amount to $380,000. These are not insignificant figures; the manufacturer of rubber goods who in these days of strenuous competition does not literally "split hairs" at his calenders is imperilling his position in the industry.

The tremendous importance of controlling the gauge of calendered materials has aroused a lively interest among engineers and this has resulted in the development of a number of different types of control. The four most widely used in the rubber industry at the present time are illustrated in the figures below.

I. Hand Gauges. No rubber factory seems to be complete without hundreds of these, and, numerically, they outweigh all others in importance. Figure 1 shows the mechanism of one of the dial types, which include Ames, Randall-Stickney, Federal, etc. The material to be measured is placed between the foot, *A*, and an anvil, *B*. When the foot is in contact with the anvil both hands of the dial are in their respective zero positions. Raising the foot by means of the lever, *C*, to introduce the sheet to be measured actuates the gear train and causes both hands to rotate. The smaller hand makes one complete revolution for four revolutions of the large hand. As ordinarily used in the rubber industry, the smallest division indicated on the large dial is .001 inch, and on the small dial 0.1 inch. Different gear ratios and scales, of course, are used for various purposes.

The dial gauge must not be considered as a direct measuring instrument in the same sense as an ordinary linear scale. The linear movement of the foot is converted, by the train of gears, to an angular motion of the dial hand. The accuracy of the indications of an instrument of this sort is dependent upon the accuracy and uniformity with which the gears are cut. It is entirely possible that the divisions in one part of the scale may not represent the same amount of travel as a corresponding number of divisions in another part, and for most accurate work the scale should be calibrated throughout, and precautions taken to avoid errors due to lost motion in the rack and pinion and gear train.

The chief sources of error in the use of this instrument are in the variations of foot pressure in different ranges of the scale and among different gauges, and in the compressible nature of the materials measured. At equal unit pressures the penetration of the foot into the sheet will be different for different stocks, and errors of considerable magnitude may result.

II. Mechanical Weighing Devices. The operation of these

is based on the relationship between gauge and weight. For a homogeneous sheet of uniform thickness and width, the weight per unit length will depend upon the specific gravity of the stock, the thickness and width of the sheet. This type of instrument must,

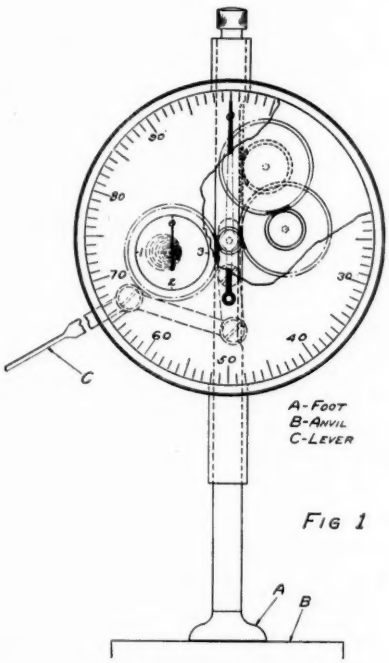


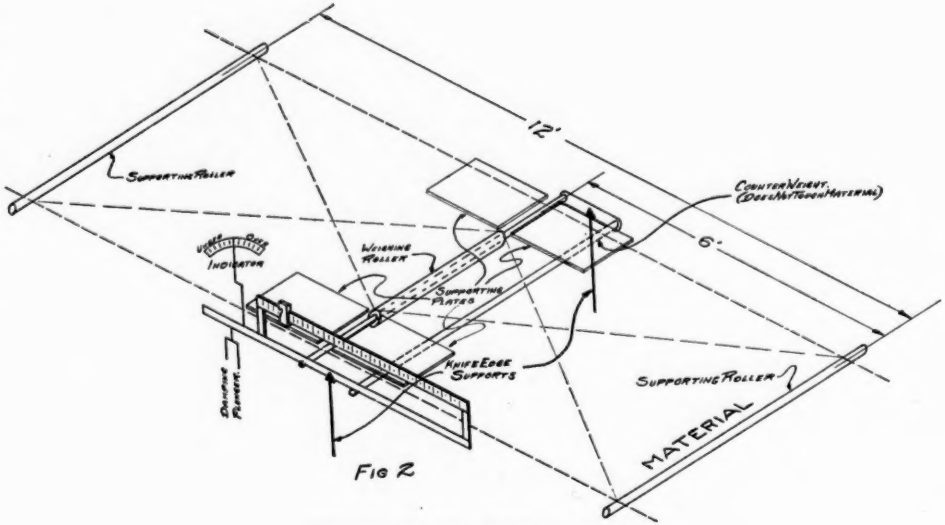
FIG 1

Dial Type Hand Gauge

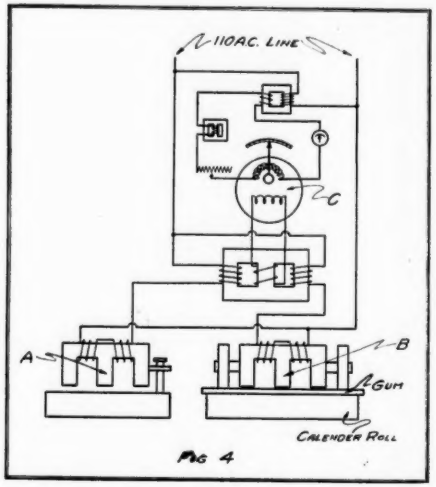
therefore, be calibrated in terms of these factors. In practice, the width of the sheet is kept constant, as described later, and the instrument is used to indicate variations in thickness through the variations in the weight of a constant length of the sheet.

Any type of weighing device may be adapted, in this manner, to the control of gauge. When so used the load pan is replaced by a roller or plate to carry the material to be measured.

Figure 2 gives the essential details of the mechanism. The double roller assembly is mounted at each end on knife edges and adjusted to incline at an angle of a few degrees with the horizontal in the direction in which the web is traveling. One end is linked with the weight beam and the indicator. The rollers at the ends are spaced equidistant from the weighing roller and the three lie in the same horizontal plane. The material passes over and is supported by the three rollers. The center roller, it is observed, has an enlarged section at the middle. This serves to carry the central strip of the material, the edges being supported on plates at either



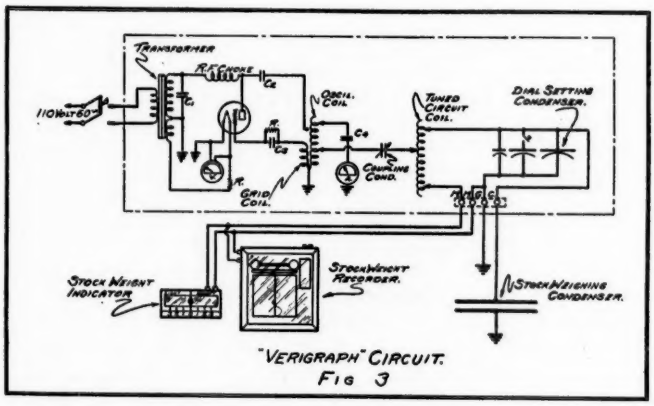
Mechanism of Weighing Device



Arrangement of Electric Currents on Magnetic Gauge

side of the enlargement in the roller, making it possible to measure sheets of various widths without adjusting the scale. In operation the counterweight is set for the proper unit area weight on the beam and the indicator then reads zero, if the weight of the material delivered by the calender is correct. If it becomes too heavy, the double roller rotates counter-clockwise, as viewed from the scale beam, causing the hand of the indicator to move toward the side of the scale marked "over," if too light it rotates clockwise toward the region marked "under." The indicator scale may be calibrated to read in fractions of an ounce over- or under-weight. Electrical contacts may be provided to indicate by lights, or other means, when the limits of tolerances have been reached, or to operate control mechanism for adjusting the calender. A graphical record of the variations may be drawn by the indicator.

The success of this system of gauging material depends upon several factors. Of first importance is the accuracy of determining the relationship between gauge and weight. This calibration, for any stock, is derived by comparing the weight of a given yardage run to constant gauge with the readings of the indicator. Knowing the variation of weight with gauge it is then a simple matter, theoretically, to estimate the uniformity of production by the use of an instrument of this sort and to make it serve as control on calender operation. Another factor of great importance is the constancy of the tension on the sheet as it passes over the weighing rollers. This may be secured by providing compensating bars before the first and after the last roll which will maintain an even tension on the web at all times. One of the most aggravating sources of error in the use of this device is the presence of drafts in the calender rooms and these cannot be avoided unless the weighed portion of the web is shielded by an enclosure. The area presented to the air is very large and a slight downward draft will throw the indicator to "over" although the weight may be correct, while an upward draft under the same circumstances will cause the indicator to read "under." In certain operations, such as tread calendering or tubing, where the



Arrangement of Electric Circuits on "Radio" Gauge

thickness is great and the width small, the latter error diminishes to negligible proportions.

III. Instruments Depending upon Electrical Principles for Indication of Gauge. These are of two classes:

(a) The "radio" gauge which operates by changes in the electrostatic capacity of part of an electrical system.
(b) The magnetic gauge, the operation of which is determined by changes in the reactance of a portion of an electrical circuit.

Both of these instruments are of recent development and application to the needs of the rubber industry. The radio gauge has been in successful use for a few years in the paper industry and has been introduced to the rubber industry during the last two years. The use of the magnetic gauge in the measurement of rubber is also a contemporary development.

Figure 3 is a diagram of the electrical circuits involved in the radio gauge. The condenser, between the plates of which the material to be gauged passes, forms part of a tuneable circuit which is inductively coupled to another circuit oscillating at about 500,000 cycles per second. The amount of current passed through the former circuit depends upon its capacity, inductance and resistance. If the latter two are kept constant and the capacity varied, a typical resonance curve is obtained the area and steepness of which are largely modified by the resistance. The steepness of the resonance curve determines the sensitiveness of the arrangment, a sharply rising curve indicating that small changes in capacity produce large changes in the current which is measured by a milliammeter used as an indicator. This method of gauging depends on the modification of the capacity of the measuring condenser by the materials passing through it. The capacity of a parallel plate condenser, such as this, is determined by the area of the plates, the distance between them and the dielectric constant of the medium separating them. The first two are maintained constant and the dielectric varied in this instrument. The space between the plates is about one-half inch. Air has a specific inductive capacity of 1, while for rubber and fabric this constant varies from about 2.5 to 4.0. Thus, when part of the air is displaced by a web of rubber the capacity of the condenser is increased. As the rubber varies in thickness, or in weight, so will the capacity, increasing with increasing thickness and decreasing as the thickness or weight diminishes. This change in capacity is reflected in the variation of the current passed through the circuit and registered by the indicator.

In practice, the electrical characteristics of the measuring circuit are chosen so that a satisfactory sensitiveness is obtained, and the indicator reads zero when a web of the proper thickness lies between the plates. Any deviations from the standard thickness are then registered by the indicator, and may be permanently recorded by an autographic recorder connected in parallel with the indicator and the chart used as a check on calender operations.

The operation of this instrument depends upon the correspondence between the thickness of the material and the dielectric effect. Since the weight of a constant area of a sheet of uniform thickness is directly proportional to the thickness, this instrument is frequently

referred to as a weight-meter, and calibration is affected by weighing known yardages of material run to a constant indicator reading.

In use a number of factors must be taken into consideration in order to insure satisfactory results. It is just as necessary here as it is in the case of mechanical scales to keep the tension on the web constant and the web parallel to the plates. Sticking of the gum to the plates must be avoided. Temperature changes will affect the separation of the plates unless compensation is provided. The manufacturers of this instrument have resorted to the use of invar for the bracket supporting the condenser plates. Line voltage changes must be without effect upon the indicator, so a voltage regulator is included in the circuit. Tube characteristics must remain constant and matched tubes are used to avoid recalibration each time a tube is replaced in the indicating circuit.

The fourth type, the magnetic gauge, as the name indicates, converts changes in thickness into magnetic effects in an electrical circuit. Figure 4 shows the arrangement of the electrical circuits. Briefly, they consist of two balanced circuits, properly adjusted regarding phase difference and power factor, one of which is maintained constant, the "master" circuit (Figure 4, A), and variations in the other (Figure 4, B) are measured by an ammeter (Figure 4, C), acting as an indicator and recorder. The measuring magnet is mounted on a carriage, riding upon the gum on the calender or idler roll, and uses the roll as an armature. When the distance between the calender roll and the magnet is the same as that between the "master" magnet and its armature the indicator reads zero. When this distance changes, the magnetic flux, and, hence, the reactance of the measuring circuit is affected and the indicator reads over- or under-gauge, depending on whether the magnet moves farther from or closer to the roll. The indicator scale may be calibrated to read directly in thousandths of an inch.

Calibration of this instrument is effected by introducing measured thicknesses of non-magnetic material between the magnet and the roll and noting the reading of the setting device when the indicator reads zero. The setting device scale may read either arbitrary divisions or be divided to indicate, directly, chosen fractions of an inch.

The accuracy of the indications of this device, as in the others, is influenced partly by the material being gauged and partly by the instrument itself. Temperature changes of the carriage require compensation, and here, again, invar is used. Line voltage fluctuations have their effect and voltage regulation is required. The softness of the stock determines the extent to which the carriage wheels sink into the sheet. Sulphur deposits collecting on the carriage wheels must be removed before they become heavy enough to affect the readings appreciably.

In a general way, the descriptions above cover the fundamental principles underlying the instruments most commonly used in gauging calendered stock and indicate the features in which the various devices excel and in which respects they are unsatisfactory. With the exception of the hand gauge all the instruments are independent of the personal equation. They are sufficiently sensitive and quick in response. All of them may easily be modified to include control of the calender. But considerable improvement is still necessary

before the ideal is reached. What is required is an instrument of adequate sensitiveness, so that important variations in gauge may be indicated and controlled. It should be unaffected by external influences such as temperature, humidity, pressure, etc. The physical characteristics of the material measured should be without effect; *i.e.*, its indications must be accurate. Its range of measurement should be large enough to include all the stocks for which gauge control is necessary. Mechanical simplicity, and portability are desirable, ruggedness is imperative. The original cost and maintenance expense should be moderate in order to allow of wide application. These are problems for the mechanical and the electrical engineer. The rubber manufacturer, on his part, can contribute to greater uniformity and economy by thorough study of the materials to be calendered and of machine operation. Progress in these directions is greatly desired.

Whether a single universal instrument can be designed is questionable. There is a strong tendency in the direction of subordinating overall gauge in some operations and relying mainly on square yard weight. In other cases gauge apparently must remain the sole factor governing the operation, so it now appears that the field may later be divided among two types of instruments, one an accurate weighing device, the other an accurate thickness measuring device.

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Essentials for Accurate Gauging for Compressible Material

By Roy W. Brown

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Abstract

Variables affecting the accurate thickness measurement of compressible sheet materials such as fabric and rubber stock are indicated as: 1. *Linear accuracy of the micrometer.* 2. *Pressure exerted by the micrometer foot.* 3. *Size of the micrometer foot.* 4. *Friction in the micrometer mechanism. A unit area foot pressure of* (70.3 *gram. per sq. cm.*) 1 *lb. per sq. in. has been found satisfactory. Friction in the micrometer mechanism is shown to limit the minimum foot pressure to approximately* (199.5 *grams*) .44 *lbs., hence a* (1.906 *cms.*) ¾" *diameter circular foot, or equivalent, is required on present available mechanical gauges.*

Methods of meeting the above fundamental requirements are indicated for optical and magnetic gauges. Limiting factors in the accuracy securable by the use of dielectric gauges are discussed. The necessity for standardized practices is so apparent as to command consideration of all concerned.

IN measuring the thickness of compressible sheet materials, such as rubber, fabric, rubberized fabrics, or any material which deforms appreciably under small loads, various factors enter the measurement in addition to the intrinsic properties of the gauge or dial micrometer uses. It is apparent that with gauges having parts which come in contact with the material being measured, deformation of the material results in an indicated thickness less than the actual thickness by the amount of the deformation. This factor has been largely responsible for the relatively inaccurate measurements secured in the rubber industry, as compared to machine shop measurements.

The effect exerted by mechanical dial micrometers has been shown for several common materials.[1] Although much research has

been devoted to more elaborate methods of gauging rubber materials, the simple dial micrometer is still used almost exclusively, with the exception of the few instances where it is desirable to measure, continuously, the thickness of moving materials.

To those who have studied the problem, it soon becomes apparent that the foot pressure of the dial micrometer must be accurately controlled, if practical accuracy is to be secured. Further, the foot pressure must also be reduced to a minimum consistent with the mechanical operation of available dial micrometers. A survey of various typical industries indicated large discrepancies in the practices as regards foot pressure. Also a survey of some 300 mechanical dial micrometers indicated a very wide discrepancy in foot pressures between different instruments of the same make, as well as between different makes. It was, therefore, thought desirable to determine the factors in dial micrometers which contribute to variable foot pressures and to determine the minimum foot pressure which could be used in a practical manner with commercially available dial micrometers. It was found that a unit area foot pressure of (70.3 grams per sq. cm.) 1 lb. per sq. in., gave readings on the majority of rubber and fabric materials within (0.051 mm.) .002 inch of the actual thickness and represented average practice of a number of the industries investigated.

A survey of the dial micrometer manufacturers indicated that with minor changes production methods would produce instruments with foot pressure of a specified value. Also a survey of a large number of different makes of new and used instruments indicated that a minimum foot pressure of (199.5 grams) .44 lb. was required to insure accurate mechanical operation of the micrometer mechanism. On this basis, with a unit area pressure of (70.3 grams per sq. cm.) 1 lb. per sq. in., it was found that a (1.906 cm.) ¾" diameter circular foot, or other shaped foot of equivalent area, was the minimum which could be used in a practical manner.

Specifications were prepared covering the above features and dial micrometers have been secured for over a period of a year complying with such specifications. Section 3, "General Requirements," Paragraph A, reads as follows: "It has been determined that to secure satisfactory service the following performance must be secured: (a) An absolute linear accuracy to within ± (0.013 mm.) .0005 in. (b) Securing and maintaining the specified foot pressure throughout the range of the gauge to within ±10% of the specified value. (c) Minimizing friction in the gauge from all causes to such an extent that its value throughout the entire operating range of the gauge does not exceed ±10% of the foot pressure," and Paragraph K, "Accuracy Tolerances," reads: "These thickness gauges shall measure linear distances to within ± (0.013 mm.) .0005 in. The foot pressure shall be within ±10% of the specified foot pressure at any portion of the range. Friction at all portions of the range, due to all causes, shall not exceed ±10% of the specified foot pressure. The face of the foot, as well as the face of the platen upon which the foot bears shall be plane and parallel to each other to within (0.013 mm.) .0005 in."

Much consideration was given to the use of dead weights to replace springs as a means of securing the desired foot pressures. An examination of available instruments indicated that a large number of these instruments had springs of such inferior design as

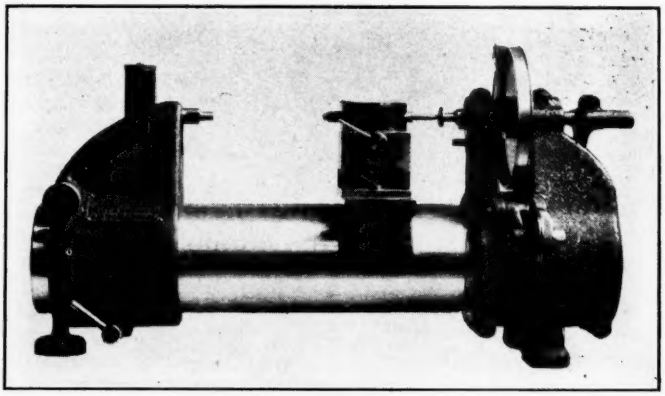

Fig. I
Precision Bench Micrometer

to cause appreciable variations between the maximum and minimum readings as well as appreciable variations throughout the useful life of the instrument. In certain instances the mounting of the springs seriously increased friction and wear in the gauge mechanism. These matters were discussed with the vendor's engineers and in several instances changes were made, which not only provided new instruments with foot pressure variation from all causes within ±10%, but insured that such foot pressures would remain within the ±10% tolerances for the useful life of the instrument. These developments largely eliminated the necessity for dead weights and provided a truly portable gauge which could be used in any position desired. Gauges with dead weights as a means of securing foot pressures have been satisfactorily used in the laboratory and other places where extreme precision was desired. It was necessary in all cases to rigidly attach these gauges to a non-movable object in such a manner that the spindle was maintained in a vertical position.

A method of comparing the linear accuracy of a dial micrometer with that of a precision bench micrometer is shown in Figure 1. Also in Figure 2 is shown a convenient and highly accurate method of determining the linear accuracy of the instrument at several points. Methods of determining friction, foot pressure and parallelism between the foot and the face upon which it bears can readily be developed to fit individual practices. The important points are: First, definite tolerances be set up for these factors; second, new gauges be secured and used instruments maintained within such tolerances.

Optical thickness gauges, as usually developed for plant service are fundamentally mechanical gauges using optical magnifying methods, therefore the remarks on mechanical gauges apply with the possible exception that due to the lesser mechanical multiplication, less friction is incurred, which permits the use of lower foot pressures. The desirability of using foot pressures lower than can be secured by first quality mechanical gauges is somewhat questionable, due to the influence of minor surface projections such as upstanding fibers in fabric and surface irregularities on rubber stocks.

Very great multiplication can be readily secured in optical

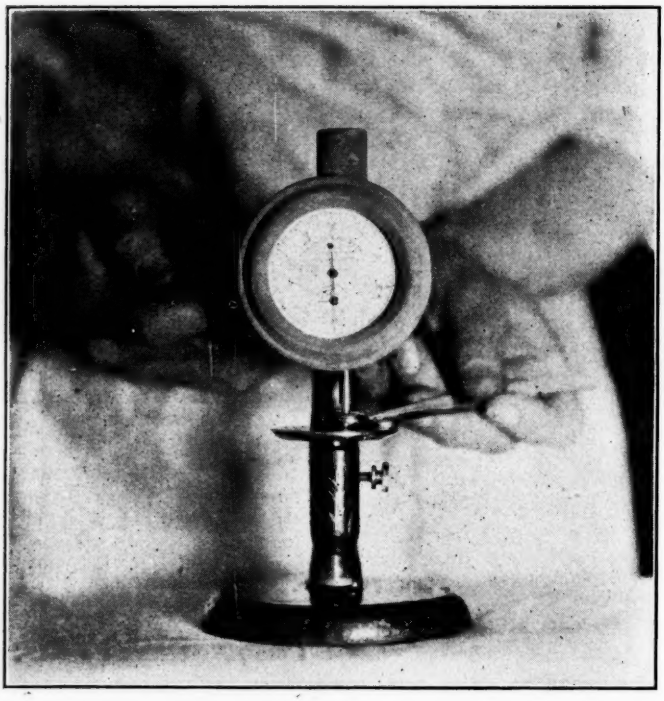

Fig. 2
Johansson type gauges are inserted in the micrometer and the micrometer readings compared to the gauging thickness

micrometers, hence the readability can be increased to any reasonable value desired. The use of two instruments of equal accuracy, but one having twice as large scale divisions as the other will result in plant practice with a far greater percentage of accurate measurements being made by the instrument having the greater readability. Accessibility, ease of use, appearance, and other similar factors will also affect the percentage of accurate measurements obtained in the plant.

Within the past several years the need for an instrument to continuously measure the thickness of moving sheet material has been realized and various instruments have been developed to accomplish this purpose, several of which have been marketed. The more accurate among these have used the gap caused by the non-magnetic material as a means of electrically determining the thickness of the material. This requires some method of support of the magnetic device on or near the surface of the moving material and hence precautions equivalent to those used with mechanical gages must be taken, if accurate indication of the stock thickness is to result. In this case since the most desirable application is at or near calenders, tubing machines or mills, variables such as temperature or plasticity, which affect the ability of the stock to resist deformation are at their worst. After considerable experimentation a method was

evolved which gave thickness indications comparable to those secured on the same stock with dial micrometers. This method consists of mounting the magnetic element as shown in Figure 3 on four wheels similar to the rear wheel suspension of a six wheel motor truck. The wheels are so proportioned and loaded that depression into the stock is a maximum of (0.076 mm.) .003 in., and the above mentioned unit area foot pressure of (70.3 grams/sq. cm.) 1 lb. per sq. in. is secured. Both experiment and extended use has confirmed the accuracy of continuous thickness indications secured in this manner. In fact, the accuracy is of the same order as is the accuracy of indications obtained in the more usual manner with dial micrometers.

In 1921 articles were published describing methods of measurement by variation of condenser capacity.[2] Numerous applications of this principle have been made among which is a commercially available instrument used to some extent in the paper and rubber industries. In this instrument the sheet material is passed between the plates of a condenser, the variation of capacity being indicated by changes of anode current from a thermionic valve in a connected oscillatory circuit. The advantages to be derived from the use of this instrument for the continuous indication of thickness of compressible material are due to the avoidance of mechanical contact with the material. Unfortunately the instrument indicates condenser capacity at the oscillation frequency and capacity is determined by many factors other than stock thickness. This accounts for the vendors' inability to calibrate the instrument directly in inches similar to all micrometers and the previously discussed magnetic gauge.

The dielectric constant and volume of the material between the plates of a condenser determine its capacity. The dielectric constant of rubber as it comes from the mills and calenders is determined by the compounding ingredients, temperature, moisture content and the frequency used in the determination.[3] Power factor affects the

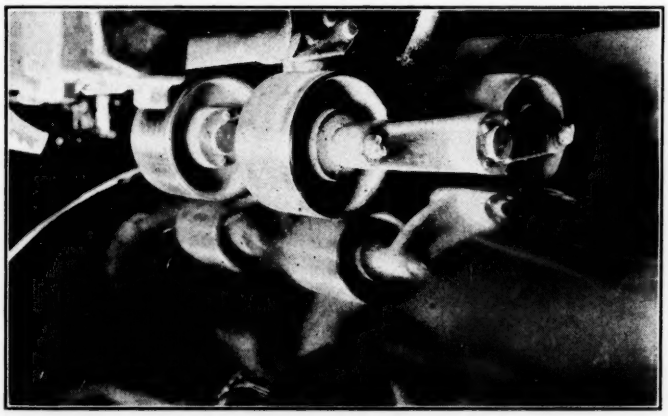

Fig. 3

Method of mounting the actuating element of continuous indicating gauge to secure foot pressure equivalent to stationary dial micrometers

frequency and must be considered. It also is a variable of the enumerated factors. It is apparent that the indication is a complex function of many factors and to be of value as a thickness indicating device these factors must be held constant within close limits. In plant practice this desired condition cannot be attained as has been proven by experiment and as is recognized by the practical production operative, hence the instrument is of service only as a transfer device and requires constant checking and intercomparison with the more conventional absolute methods of thickness measurement or weighing.

Another method which offers possibility of combining the advantages of the magnetic and dielectric type gauges was suggested by H. A. Thomas in 1923.[4] This method uses a high frequency oscillating circuit, but depends upon an inductive shunt rather than capacity variation, thereby securing freedom from a number of instrumental errors inherent in the dielectric instrument.

The economic desirability of uniformity of measurement of the constituent parts, as well as the completed article of manufactured rubber and cotton materials is acknowledged by all. To secure even remote approach to the uniformity already attained on metallic machined articles requires compliance with the essentials discussed and rigid observance throughout the plant of a carefully prepared measurement technique. It is hoped that a more general recognition of the fundamentals of accurate measurement of compressible materials will result in a standardization of such important factors as foot pressure.

NOTES

1. *India Rubber World,* July 1, 1927, pp. 197-198.
2. *Engineering,* Sept. 9, 1921, and *Machinery* 28 No. 1, pp. 36-37, Sept., 1921.
3. *International Critical Tables,* Vol. II, pp. 273-274.
4. *Engineering* 135, pp. 138-140, Feb. 9, 1923.

[Reprinted from THE RUBBER AGE (N. Y.), Vol. 29, No. 9, August 10, 1929]

The Double Refraction of Stretched Rubber*

By W. C. Van Geel and J. G. Eymers

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Abstract

A relation between the double refraction and the elastic tension of rubber is derived. The formula which is given defines double refraction as a function of tension up to a certain limiting value of the tension, at which point a strict proportionality between double refraction and tension begins. At this limiting tension the elongation is 70 per cent., and it is noteworthy that at just this elongation X-ray photographs of rubber begin to show fibre diagrams.

THE double refraction of stretched rubber has already been measured by Bjerkèn[1] and by Rossi[2], who found no general law which would show the way in which double refraction depends upon the tension.

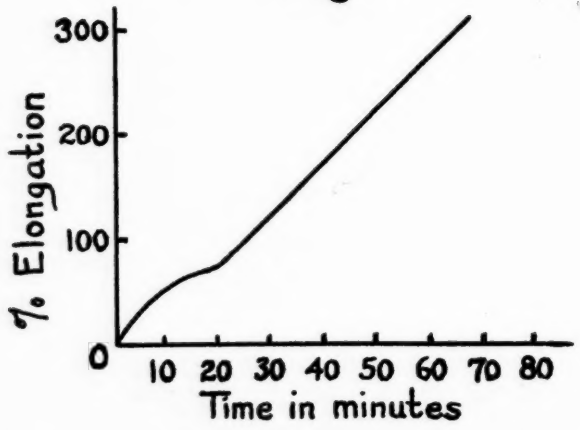
It seemed therefore that it might be of value to obtain precise measurements again, particularly since it has now become technically possible to prepare rubber which absorbs only a little light, so that it is no longer necessary to work with very thin sheets.

The measurements were begun with raw plastic rubber, which was milled into thin sheets. Subsequently rubber obtained by the evaporation of pure latex was tested.

First of all it is necessary to distinguish between plastic and

*Translated from Zeitschrift für Physikalische Chemie, Vol. 3, No. 3, pages 240-246, May 1929.

Fig. 1



elastic rubber. By plastic rubber is meant a rubber which when subjected to stress, in the manner described below, shows no ultimate deformation but whose elongation is a function of the time, the effect being a "flow." By elastic rubber is meant a rubber which under a given stress shows after a brief time a definite deformation. When the tension is released, elastic rubber resumes in a short time its original condition, whereas plastic rubber remains in its deformed state and only after a long time, often after days, returns to its original state.

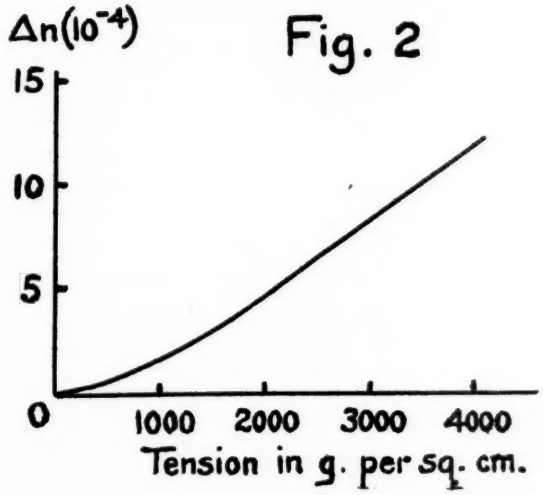
Plastic Rubber

In the case of plastic rubber the elastic properties were first of all investigated. A small rectangle was drawn with ink on the sample. The latter was then suspended in a rack and loaded with definite weights by means of a scale pan.

The changes in length and width of the rectangle and in the thickness of the samples at definite loads were measured. It was found that the length, width and thickness changed with time when the pan was loaded with a constant weight. No equilibrium was reached, and the rubber continued to stretch until it broke. Only at very small loads was an equilibrium reached. Fig. 1 shows the change in length with time. At the beginning when the rubber is still elastic, the increase in length and the decrease in thickness and width are linear functions of the time.

The double refraction was measured by means of a Babinet compensator. The source of light was a mercury vapor lamp, from which the green light was removed by a filter.

Fig. 2 shows the double refraction as a function of the load per square centimeter (tension). Except at the beginning at low tensions when the rubber is still elastic, the double refraction is a linear function of the tension. Plastic rubber shows therefore a certain resemblance to a liquid for, as is known, certain liquids under tension show a double refraction which is proportional to the tension. Since these phenomena are not of direct interest in the



present problem, further measurements were made with elastic rubber.

Elastic Rubber

Very elastic rubber was obtained by drying latex. Under stress, the length, width, thickness and double refraction changed only during the first moments. Equilibrium was reached in a short time, which depended upon the stress, but which never exceeded three minutes even with high loads.

Fig. 3 shows the change in the length with the time. With elastic rubber, the measurements could be made under well defined conditions, and measurements of the double refraction as a function of the tension had some significance. A new sample sheet of rubber was used for every measurement, for after a strip had once been stressed, it showed on being stressed again a greater double refraction than did a fresh sample under the same tension.

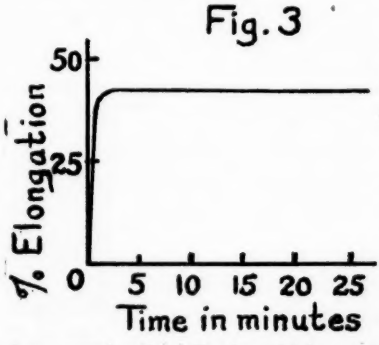


Fig. 4 shows the results of these measurements. The mathematical sign of the double refraction is positive. The curves in Fig. 4 are for strips of different thicknesses. The magnitude of the double refraction per unit of thickness obviously depends upon the original thickness, because of the presence of an oxidized layer on the surface of the rubber. As a result, the effective thickness is measured disproportionately high.

The curves may be altered by proportional changes in their

ordinal values to allow for the inaccurate measurments of thickness, but this does not change their form, and the double refraction is known only within a certain precision.

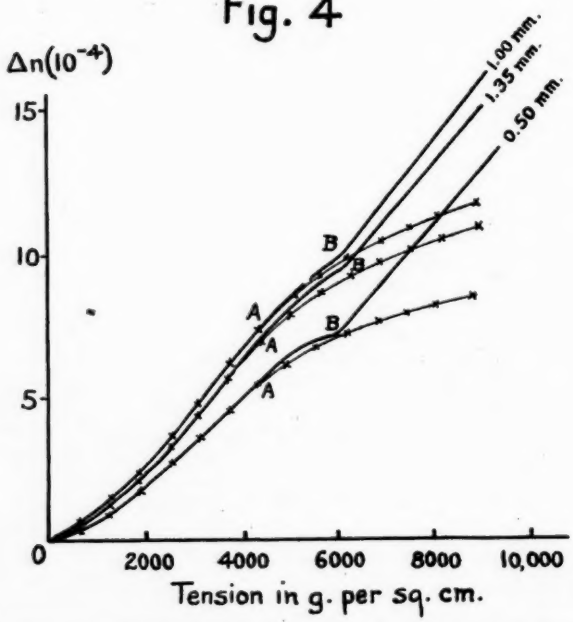
The form of the curves is the essential feature, and it is significant that their form is very similar to that of curves showing the relation between the double refraction and field strength of liquid crystals in a magnetic field. This relation has been derived by Ornstein[3] and is represented by the equation:

$$\Delta\Sigma = A\left(1 - \frac{3}{b}\coth b + \frac{3}{b^2}\right)$$

where $\Delta\Sigma$ is the change in the double refraction $b = \frac{\mu H}{kT}$, where in turn μ is the magnetic moment of a particle of the liquid-crystalline substance, H is the magnetic field, k is the Boltzmann constant, T is the absolute temperature, and A is a constant.

Ornstein developed this formula on the basis that liquid crystals are composed of anisotropic molecules which in the magnetic field become aligned in parallel formation. This alignment of anisotropic

Fig. 4



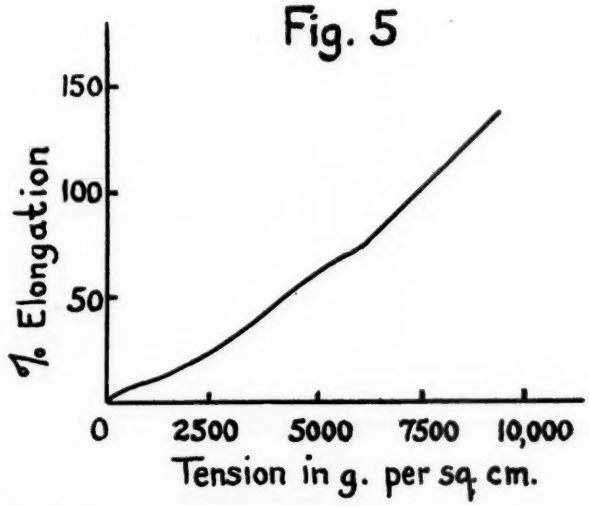
molecules probably takes place in rubber when the latter is stretched. In this case b in the formula above can be assigned a value proportional to the tension (at constant temperature). In Fig. 4 a theoretical curve for each thickness is recorded[4].

It is evident that the form of the theoretical curves conforms to that of the experimental curves up to a certain limit (B in the Fig.). At B the linear relation between double refraction and tension begins, as with plastic rubber. The deviation of the curves in the

range from A to B probably depends upon the fact that the new condition which is fully evident at B is previously effective to a small extent.

With every sample the linear relation began at the same tension (approximately 6 kg. per sq. cm.), regardless of the original thickness of the samples. From this point on, the length, width, thickness and double refraction again varied with the time, just as with plastic rubber.

The elongation in centimeters as a function of the tension was measured at the same time, the results of which are shown in Fig. 5. The form of the curve is somewhat similar to that of the curves in Fig. 4. Here, too, a linear relation begins at a tension of 6 kg. per sq. cm., in this case between elongation and tension. At this point the elongation of every sample was approximately 70 per cent.



With plastic rubber, the linear relation also began at 70% elongation, but here the tension was very small.

This limiting value of 70% elongation appears therefore to be a *characteristic constant of pure rubber.* It probably depends upon the composition of the rubber and upon the temperature.

It is worthy to note that in X-ray photographs of rubber at elongations below 70 per cent., Katz[5] found only an amorphous ring, while above this elongation (*i. e.,* in the range where a linear relation was found in the present work on double refraction) crystal interferences appeared, the intensity of which increased with the elongation.

Another remarkable property of plastic rubber should be noted. When a strip of rubber is stretched beyond its limiting point of flow and is then held at constant length, the double refraction diminishes with time. It does not disappear however, and a residual double refraction remains present. This is also true of the tension. The remarkable fact is that this residual double refraction and residual tension are almost or wholly independent of the original elongation.

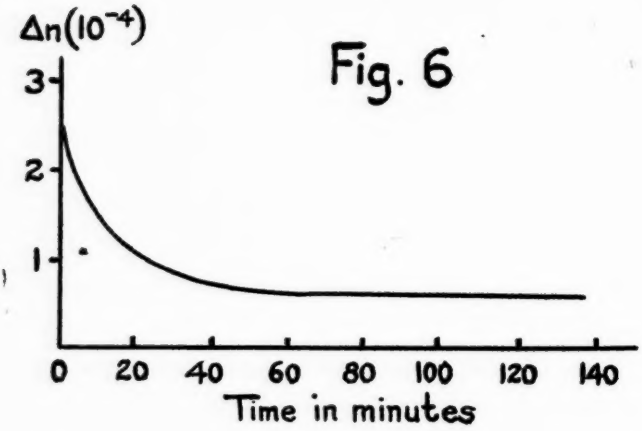


Fig. 6

The diminution in the double refraction with time is shown in Fig. 6.

It is hoped that the work described above offers an exact experimental demonstration of the relation between the double refraction and elongation of pure rubber. Investigations of the evolution of heat during the elongation of rubber will be described in a forthcoming paper.

Acknowledgment is made to L. S. Ornstein for his help and interest, to A. van Rossem for supplying the rubber, and to J. R. Katz for making the work possible and for his valuable advice.

Notes

1. *Ann. Physik* **43**, 808 (1891).
2. *Rend. Napoli* [3] **16**, 125, 142 (1910).
Cimento [5] **20**, 226, 268 (1910); [6] **2**, 151 (1911).
Beibl. Physik **35**, 206, 364; **36**, 67.
Fortschritte Physik **2**, 394 (1910).
3. *Ann. Physik* **74**, 445 (1924).
4. This form of the double refraction curve is also found for stretched celluloid. See Ambron-Frey, *Polarisationsmikroskop*, 175.
5. *Naturwissenschaften* **1925**, 110.

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The Consumption Of Accelerator During Vulcanization

L. v. Wistinghausen

THE so-called chemical theories of acceleration are based on the transformation of the accelerator during the process of vulcanization, but the quantitative study of such reactions is confronted by tremendous difficulties. From the increase in the amount of combined sulfur with time of cure, Hardman and White[1] have drawn conclusions as to the relative stability of various accelerators. In these experiments they chose conditions which were specific for each accelerator, affording optimum effects.

In the following work an attempt has been made to obtain some insight into the fate of the accelerator in the course of heating by a quantitative estimation according to the methods described below of the amount of accelerator found in the acetone extract of vulcanizates with increasing time of cure.

In order to study the effect on the accelerator of various ingredients, the type of raw rubber, the quantity of sulfur, and the addition of fillers were considerably varied, while the ratio of accelerator to rubber remained constant.

Attention was first directed to vulcanizates containing diphenylguanidine or mercaptobenzothiazole, as in these cases a quantitative estimation of the amount of accelerator remaining could be expected. The same experimental conditions were used for both accelerators, as it was interesting to determine to what extent their known differences could be expressed by their manner of disappearance. A technical point of view was left entirely out of the question, hence

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*Translated from Kautschuk, Vol. 5, Nos. 3-4, Pages 57-61, 75-77, Mar.-Apr. 1929, by J. P. Fahy.

the physical optimum was often far exceeded in the time of heating as is evident from the stress-strain curves of the vulcanizates.

Procedure

The finely ground material (20 g.) was extracted with acetone in a Soxhlet apparatus for twelve hours, and the acetone was then completely evaporated from the extract on a steam-bath.

Determination of Diphenylguanidine

The residue is dissolved in ether, and 10 cc. of O.1*N* aqueous hydrochloric acid added. The ether is then evaporated, and the cold hydrochloric acid solution containing now a part of the D. P. G. is filtered through a wet filter. The portion insoluble in hydrochloric acid is again dissolved in ether, treated with 10 cc. of O.1*N* HCl, and so forth. After this operation is repeated three times and the filter washed with water, all the D. P. G. has been transferred to the hydrochloric acid solution. To the combined filtrates, not exceeding 50 cc. in volume, there is added 50 cc. of a 1% aqueous picric acid solution (precipitation according to the method of Callan and Strafford), the flask is rotated a few times until the yellow precipitate has flocked together, and then allowed to stand over night. The precipitate is filtered off on a Gooch crucible which has been lined with filter paper, dried at 100° C. and weighed. The crystals adhering to the glass walls are transferred to the crucible with the help of the filtrate, the precipitate is washed once with 5 cc. of water, and dried at 100° C. to constant weight. The weight of the precipitate multiplied by the factor 0.4798 gives the amount of diphenylguanidine present.

Parallel determinations with pure diphenylguanidine differed not more than 1%. The limit of error using vulcanizates must be placed at ±3%. Vulcanizates heated for a rather long time give picrates which apparently contain besides D. P. G. decomposition products, as they become dark brown on drying and melt at a very low temperature, though not below 100° C.

Determination of Captax (mercaptobenzothiazole)[2]

The dried acetone extract is dissolved in 20 cc. benzene with the aid of heat and filtered. The flask is washed twice with 10 cc. portions of benzene, and to the combined filtrates there is added a 3% filtered solution of copper oleate (De Haën) in benzene in excess so that the solution remains green. The flask is allowed to stand over night, and then the orange-yellow precipitate is centrifuged off, washed first with benzene and then with petroleum ether while in the centrifuge, dried at 140° C. and weighed.

The following reaction is involved:

$$\underset{\text{Captax}}{2C_7H_5NS_2} + \underset{\text{copper oleate}}{Cu(C_{18}H_{33}O_2)_2} \longrightarrow \underset{\text{oleic acid}}{2C_{18}H_{34}O_2} + \underset{\substack{\text{copper}\\\text{salt of}\\\text{Captax}}}{CuC_7H_4NS_2} + \underset{\substack{\text{½ dibenzo-}\\\text{thiazoledi-}\\\text{sulfide}}}{C_7H_4NS_2}$$

The cupric salt of mercaptobenzothiazole which forms at first and which is soluble in benzene changes to the insoluble cuprous salt and dibenzothiazoledisulfide (similar to the decomposition of cupric

cyanide to cuprous cyanide and cyanogen). The precipitate contains therefore exactly half the Captax present; its weight represents 68.7% of it, and hence is to be multiplied by the factor 1.4556. The error here is about the same as in the determination of diphenylguanidine as the picrate.

Effect of Time of Heating

Cures were run of each mix at 4 at. for 5, 10, 20, 30, 60 and 90 minutes. In almost all cases the heating caused a decrease in the amount of accelerator remaining as found by extraction. A minimum value of 1.5% of the accelerator added was found in one case of a 90-minute cure. In this way curves were obtained showing the consumption of added accelerator in per cent. These will be discussed in detail.

The Base Mix

The base mix, from which the other mixes were obtained by changing the quantity of some ingredients and adding others, consisted of:

Raw rubber (first latex crepe)	100 parts
Diphenylguanidine or Captax[3]	1.4 parts
Thermatomic carbon	38.5 parts
Sulfur	3.8 parts
Zinc oxide	None

The corresponding curves are given in Figure 1. The consumption of more diphenylguanidine than Captax agrees with the greater vulcanization effect in such unusual compounds. Figure 2 shows the stress-strain curves.

Varying the Type of Raw Rubber

In place of first latex crepe, sprayed rubber and Peru rubber were used. The marked deviations in the position and course of the consumption curves (D. P. G. Fig. 3, Captax Fig. 5) are doubtless due to the marked differences in the powers of absorption of the various rubbers. Sprayed rubber showed the least requirement of either accelerator. In the D. P. G. compounds the vulcanization

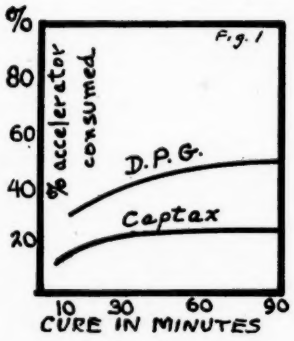

Fig. 1
Consumption of accelerator in base mix (First Latex Crepe)

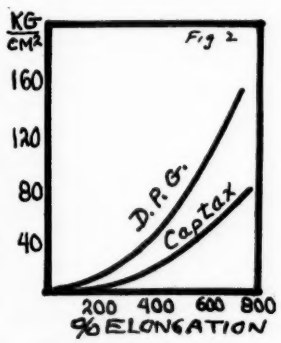

Fig. 2
Stress-strain curves (20 min. cure)

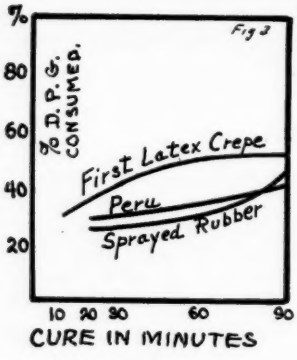

Fig. 3
Accelerator consumption
Base mix + Diphenylguanidine

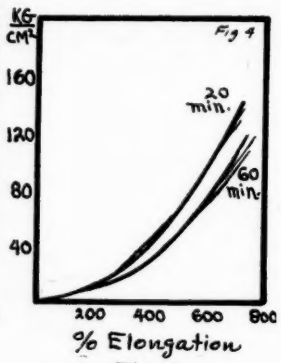

Fig. 4
Stress-strain curves

effect was the same for all three rubbers, and the stress-strain curves for 20 and 60 minutes are close together (Fig. 4).

Effect of Zinc Oxide

Cures were made of the original base mix (first latex crepe, diphenylguanidine) with the addition of 0.2% to 98% of zinc oxide calculated on the rubber. The 0.2% had no noticeable effect, but 0.75% greatly increased the consumption of accelerator. The increase is relatively large using small amounts of zinc oxide, falling off with further additions, and at about 12% zinc oxide approaching a logarithmic curve with the maximum consumption of D. P. G. as a limit. (See Fig. 6.)

The consumption of accelerator is somewhat less with larger amounts of zinc oxide, the cure being 30 to 90 minutes. Figure 8 shows the result of adding about 12% zinc oxide. The deviations between the various types of raw rubber are greater than in the case of the zinc free compounds. The consumption of accelerator is largest in the case of first latex crepe, and least in the case of sprayed rubber probably because of the presence of the natural basic accelerator; the Peru lies in between. Table I shows the trend in the consumption of accelerator with increasing amounts of zinc oxide.

Table I

CONSUMPTION OF D. P. G. IN PERCENT

Cure in minutes	*Amount of Zinc Oxide Added*			
	12%	24.5%	49%	98%
10	36			
20	50			52
30	63	64		64
40			73	73
60	86		83	83
90	90	85	84	84

Figure 7 shows the change in the angle of curvature of the stress-strain curve using 12% zinc oxide as compared with the zinc-free base mix.

The curves showing the consumption of D. P. G. are more nearly

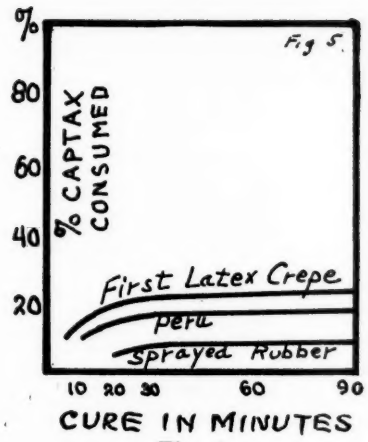

Fig. 5

Accelerator consumption
Base mix + Captax

straight lines in the case of sprayed rubber and Peru rubber than in the case of the first latex crepe, at least within the limits investigated. Here, too, the stress-strain curves fall close together as in the case of the zinc-free compounds. Figure 9 shows the 20- and 90-minute cures.

In the corresponding Captax compounds containing 12% zinc oxide, the three types of raw rubber differed in the consumption of accelerator (Fig. 10). In the case of the Peru rubber, the consumption was abnormally high and was accompanied by a marked undercure, so that a side reaction must have played a part, resulting in the formation of a zinc salt. (See Fig. 11.) Likewise the stress-strain curves of the first latex crepe and sprayed rubber compounds do not coincide, the greater consumption of Captax by sprayed rubber being reflected in a higher cure. (Fig. 10, 11.)

Varying the Amount of Sulfur

Attention was now directed to vulcanizates with the same composition as the base mix but with a smaller (1.9%) or larger (7.5%) percentage of sulfur calculated on the rubber, and both without and with the addition of zinc oxide (12%).

The Effect of Sulfur Without Zinc Oxide

The consumption of D. P. G. was about the same as in the case of 3.8% sulfur. This was true of all three rubbers as is shown by Table II.

Although the stress-strain curves (Fig. 12, 13) show an increase in cure with increased sulfur, yet this need be ascribed only to a very slight extent to the participation of the accelerator in the reaction. This is more clearly shown in the corresponding zinc-free Captax compounds (Fig. 14, 15). In the case of 1.9% and 3.8% sulfur, the consumption curves lie close together, and in the case

Table II

PERCENT. OF DIPHENYLGUANIDINE CONSUMED

%S	*Cure in minutes*	*First latex crepe*	*Sprayed rubber*	*Peru*
1.9	10	27		
	20	35	24	28
	30			
	60	46	32	33
	90	52	46	34
3.8	10	29		
	30	39	25	29
	60	46	30	33
	90	53	45	38
7.5	10	36		
	30		27	
	60	46	30	34
	90	54	42	

of 7.5% sulfur the consumption of accelerator is still smaller, while the cure increases with the sulfur (Fig. 16, 17). The cure of the compounds rich in sulfur was retarded, though accelerator was present, by direct action between the rubber and the sulfur (the consumption of Captax in the case of sprayed rubber containing 7.5% sulfur was nil). Consequently the compounds showed a slower increase in tensile, the optimum being reached only after 30 to 60 minutes cure (Fig. 18, 19), in contrast to the Captax compounds containing zinc oxide.

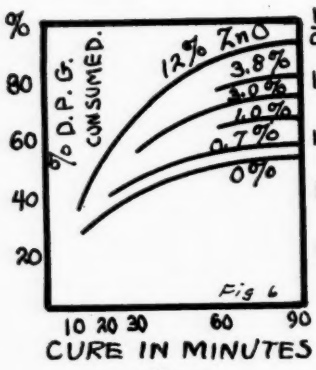

Fig. 6

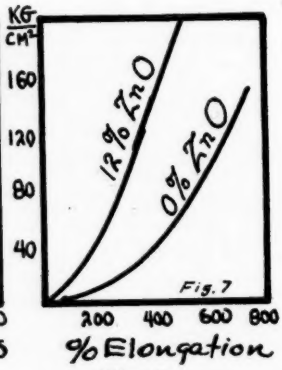

Fig. 7
(20 min. cure)

First Latex Crepe + ZnO + Diphenylguanidine

The Effect of Sulfur in the Presence of 12% Zinc Oxide

The consumption of diphenylguanidine was decidedly less using 1.9% sulfur than using 3.8% sulfur, and decidedly more using 7.5% sulfur. The curves for the three types of raw rubber are given in Fig. 20 and 23.

The effect of doubling the quantity of sulfur, that is, the distance between the curves representing the 1.9%, 3.8%, and 7.5% sulfur, is

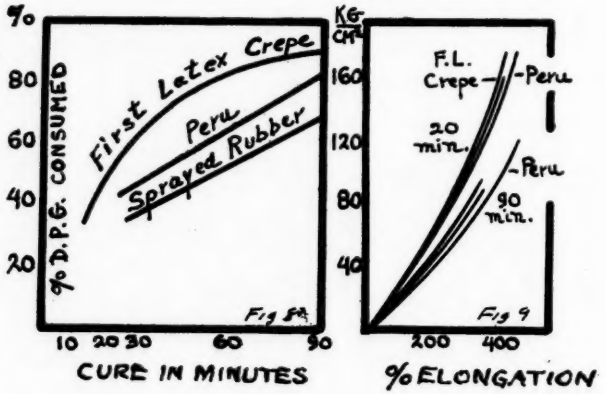

Fig. 8
Accelerator Consumption
D.P.G. (F. L. Crepe, Sprayed Rubber, Peru) 12% ZnO

Fig. 9
Stress-strain curves

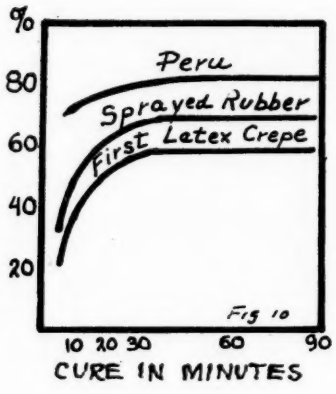

Fig. 10
Consumption of Accelerator

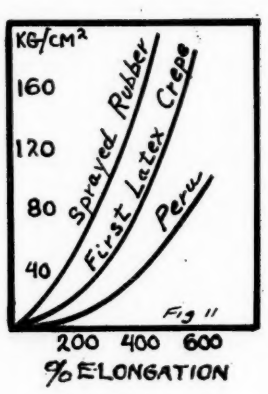

Fig. 11
Stress-strain curves
for 10 min. cures
Captax, (First Latex Crepe, Sprayed Rubber) 12% ZnO

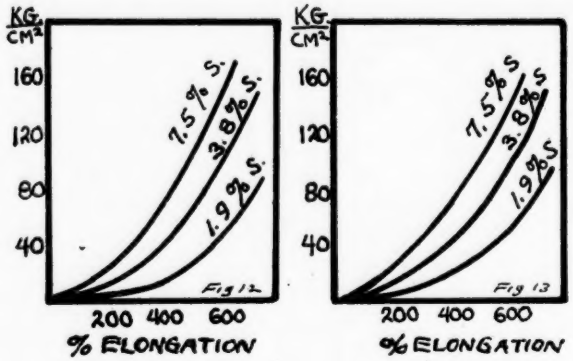

Fig. 12 Fig. 13

Stress-strain Curves, 20 min. cure

First Latex Crepe + D.P.G. Sprayed Rubber + D.P.G.

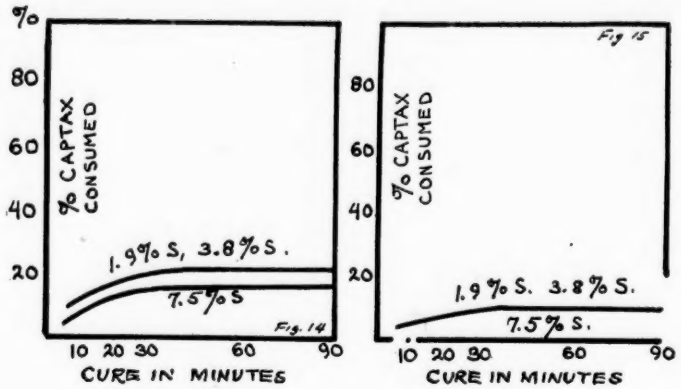

Fig. 14 Fig. 15

Consumption of Captax

First Latex Crepe Sprayed Rubber

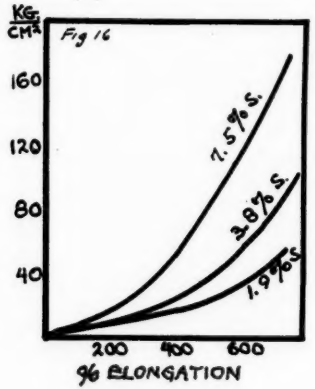

Fig. 16

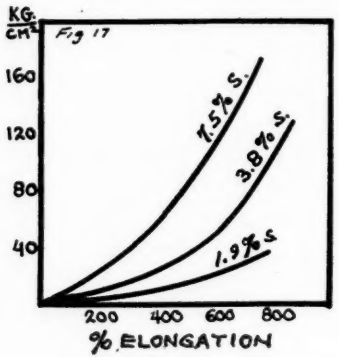

Fig. 17

Stress-Strain Curves for 30 min. Cure
Captax

First Latex Crepe — Sprayed Rubber

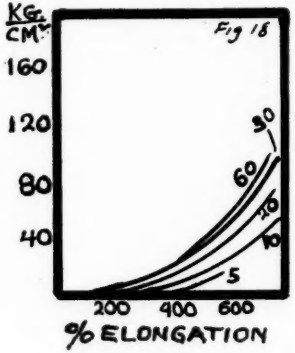

Fig. 18

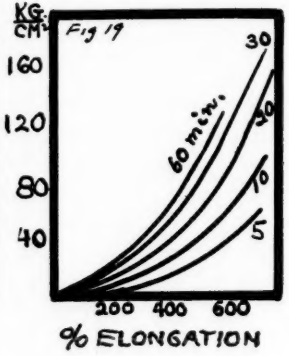

Fig. 19

3.8% S — 7.5% S

Stress-strain curves
First Latex Crepe, Captax

least in the case of sprayed rubber, no doubt due to the presence of the natural accelerator, and greatest in the case of Peru rubber.[4]

The stress-strain curves (Fig. 21, 22, 24) show that with increased sulfur there is an increase in cure, which somewhat parallels the accelerator consumption. Therefore in these ZnO compounds, the accelerator must have participated in the reinforcement obtained by increasing the sulfur. Moreover the optimum cure was generally reached in twenty minutes. (Fig. 25, 26, 30.)

The phenomena noted, using any of the three types of raw rubber with D. P. G., are much the same in the case of Captax and first latex crepe. (Accelerator consumption, Fig. 27; stress-strain curve, Fig. 28.) Sprayed rubber and Peru, however, show no marked increase in the consumption of Captax with increased sulfur.

Fig. 27 also shows very well the well known differences in the activity of D. P. G. and Captax as regards the accelerator consumption. All the Captax curves rise more sharply over the period 5 to 20 minutes than the corresponding D. P. G. curves; they then fall off toward the horizontal axis, crossing the D. P. G. curves. The steeper initial rise of the curve corresponds to the tendency of the accelerator to cure sooner. The flat character of the latter part of the curves is worthy of notice.

However, in the case of the compounds investigated, the attainment of the maximum consumption value did not coincide with the best technical cure. On the contrary, the consumption curve, after passing the point of optimum cure (5 to 10 minutes in the case of Captax, and 20 to 30 minutes in the case of D. P. G.), continues on, without any noticeable change in direction, through the zone of reversion (Fig. 29), and therefore a certain parallelism between this further consumption of accelerator and its "devulcanizing" action is hardly mistakeable. Thus, in the Captax compounds, except in the case of sprayed rubber containing natural accelerator, when the maximum consumption was reached the stress-strain curves for the 60- and 90-minute cures lie close together; and likewise in the D. P. G. compounds the displacement of the stress-strain curves seems to follow the trend of the consumption curve, corresponding to the type of rubber used. (Fig. 25, 26, 30.)

The Effect of Fillers on the Extraction of the Accelerator

From a compound consisting of

Rubber	100 parts
D. P. G.	1.4 parts
Sulfur	3.8 parts

it was possible to extract after a five and ten minutes cure 63% and 61%, respectively, of the added accelerator. The addition of 38.5% of Thermatomic carbon caused no noticeable decrease in the percent of accelerator extractable, but the addition of other blacks did. (Table III.)

Table III

% Black Calc. on the Rubber	*D. P. G. Remaining After a 10-Minute Cure*
19% Thermatomic	60%
38% Thermatomic	60%
42% Micronex	37%
42% D F special black	27%
42% R Z lamp black	47%

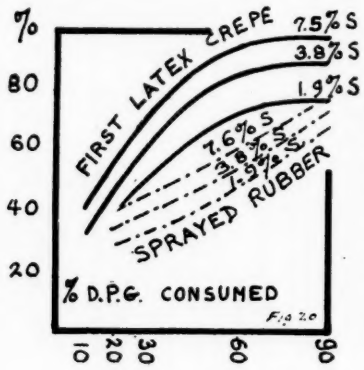

Fig. 20
Accelerator consumed
Diphenylguanidine, 12% ZnO.

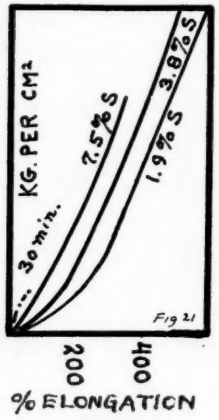

Fig. 21
Stress-strain curves
F. L. Crepe

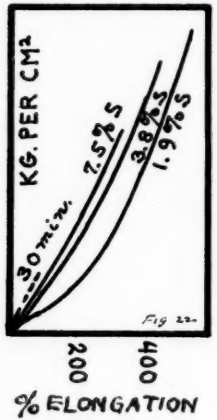

Fig. 22
Sprayed rubber

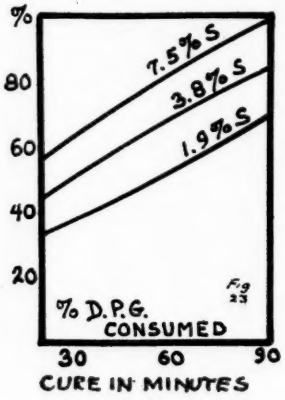

Fig. 23
Accelerator consumed
Peru, Diphenylguanidine, 12% ZnO.

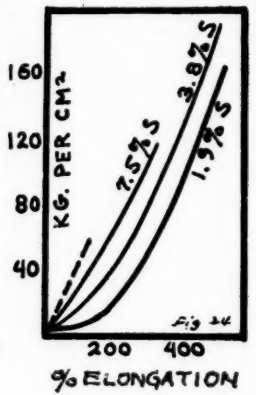

Fig. 24
Stress-strain curves

This phenomenon may be ascribed to the different absorptive capacities of the various blacks,[5] a function which is approximately proportional to the degree of fineness. In the case of Thermatomic carbon, adsorption is hardly noticeable, so that its general use is thereby facilitated.

The type of zinc oxide used was varied (preceding formula +126% ZnO), and 5- and 10-minute cures run, but no noticeable

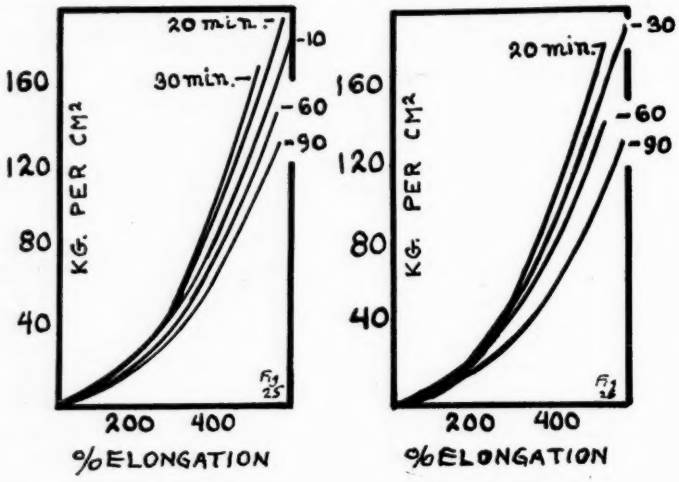

Fig. 25 **Fig. 26**

Stress-strain Curves

First Latex Crepe **Sprayed Rubber**

1.9% S, D.P.G., 12% ZnO.

differences in the vulcanizates could be detected (Table IV), as the D. P. G. salts, such as the sulfate, which were finally formed were extractable with acetone.

Table IV

% ZnO Calc. on the Rubber	*D. P. G. Remaining After a 10-Minute Cure*
126% "A"	53%
126% "B"	59%
126% "C"	52%
126% "D"	49%

The experiments show that the action of either accelerator is not purely catalytic but is accompanied by a consumption of accelerator, which to a certain degree is proportional to the results obtained. Where no accelerator to speak of was consumed, no acceleration in cure occurred. In the disappearance of the accelerator, thermal decomposition can be involved only to a very slight extent, as pointed out by Naunton (*Chem. Centralblatt,* II, 1315 (1925)) among others. Sebrell and Vogt (*Chem. Centralblatt,* I, 169 (1925)) assume that a reaction takes place between zinc oxide and diphenylguanidine.

The formation of complex compounds by different accelerators

with cobalt salts of unsaturated organic acids[6] by merely bringing

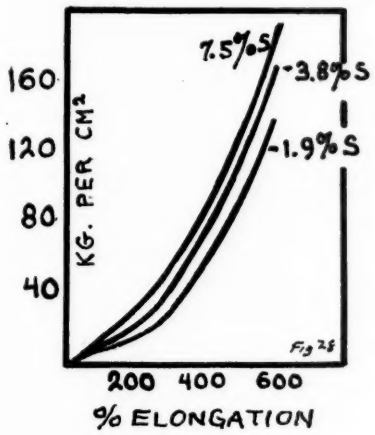

Fig. 28
Stress-Strain Curves
First Latex Crepe
Captax, 12% ZnO.

the components together makes it probable that the compounds of D. P. G. or Captax with zinc oxide or zinc salts are also of a complex nature. Such compounds on the one hand might increase the solubility of the accelerator in rubber diphenylguanidine is

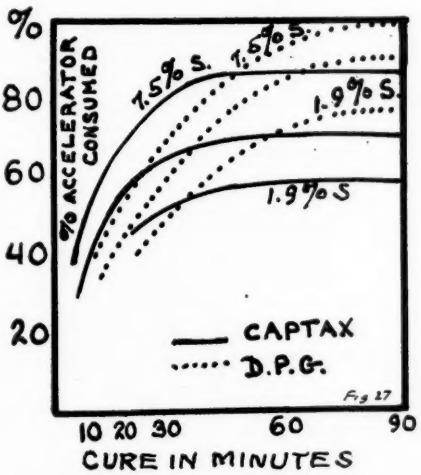

Fig. 27
Accelerator Consumption Curves
First Latex Crepe
12% ZnO.

more soluble in petroleum ether as the cobalt complex than alone), and on the other hand they might emphasize the electro-positive character of the central zinc atom and thereby assist in the activation of the sulfur.[7]

The limit in the consumption of accelerator reached in the presence of 12% zinc oxide might depend on the solubility limit of the zinc-accelerator compound. However, the accelerator even in combination would be extractable by acetone.

The final change in the accelerator molecule must therefore be ascribed to the action of the sulfur on the zinc-accelerator complex. This is also indicated by the increased consumption of accelerator (increase in limiting amount) obtained with increase in sulfur.

Moreover, a compound between the accelerator and the rubber molecule would be plausible.

The question, what is the relationship between the accelerator consumption curve and the curve representing the combined sulfur, can be answered only by further experiments. According to Hardman and White (*loc. cit.*) D. P. G. and Captax are so-called semi-permanent accelerators, which, with increase in combined sulfur, yield curves concave to the time axis. The degree of curvature of the consumption curve in the case of D. P. G. appears dependent on the type of raw rubber, and even more so in the case of Captax; the slowing up of the reaction is not due to the disappearance of the accelerator—on the contrary, Captax, even at temperature above 150° C., appears to be very stable in rubber compounds.

With regard to the combined sulfur, it has been shown (see also Twiss *loc. cit.*) that it increases continuously without any point indicating the position of optimum cure. The likewise continuous trend in the curve representing the accelerator consumption confirms

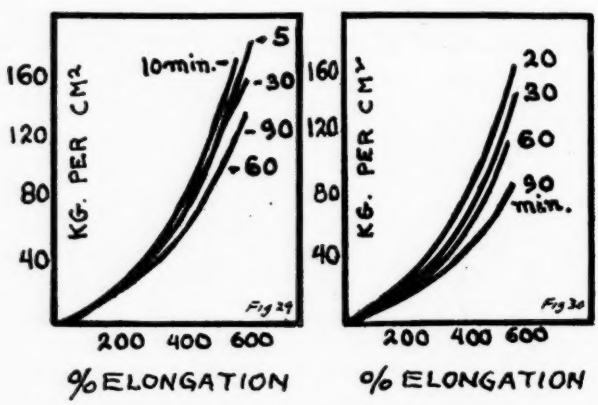

Fig. 29 Fig. 30

Stress-strain Curves

First Latex Crepe Peru

Captax, 12% ZnO, 3.8%S D. P. G., 12% ZnO, 1.9%S

the fact that the optimum technical cure does not represent a state which can be physically or chemically defined, thus agreeing with the microscopic findings of Pohle (*Chem. Centralblatt* I, 2609 (1927)).

NOTES

1. *Gummi-Ztg.* **1927,** 305.
2. This method is suitable as a qualitative test for Captax in cured rubber. It is advisable to extract a 100 g. sample. By this method Captax was shown repeatedly to be present in Goodyear treads and whole tires. By analyzing the corresponding cuprous salt it is not a difficult matter to show which thiazole derivative is present.
3. Stearic Acid was not used with Captax, as a new variable would thereby be introduced. The comparison of D.P.G. and Captax should be made using the same type of raw rubber. However, the experiments show that different raw rubbers differ distinctly in their effect on the quantity of accelerator extractable. In the case of Captax, the addition of fatty acid would have brought about conditions similar to those present using another raw rubber with a different fatty acid content, thereby hindering the comparison of D.P.G. and Captax.
4. Although decided overcures are obtained with 7.5% sulfur and 30 to 90 minutes cure, yet the accelerator content is much greater in the case of sprayed rubber than in the case of first latex crepe (Fig. 20).
5. Similar to the effect of gas black on free sulfur, observed by Twiss (*Gummi-Ztg.* **1928,** 2307).
6. A beautiful demonstration of these complex compounds accompanied by color reactions may be obtained in associating organic media (such as benzene, benzine, petroleum ether, chloroform, carbon tetrachloride, carbon disulfide, and sol-rubber—dissociating solvents such as alcohol, ether, and pyridine are to be avoided), if one dissolves about 0.2 g. of the accelerator in question in one of the solvents advised in a test tube, and adds drop by drop a benzene solution of the cobalt salt (De Haën) of linoleic, oleic, or resinic acid until the color which appears increases no further. The following colors are obtained:

Diphenylguanidine	violet
Orthotolylguanidine	vermillion
Hexamethylenetetramine	grayish-violet with tinge of green
Zinc dithiocarbamate (dissolved in benzene-acetone or benzene-alcohol)	bright blue
Zinc orthobutylxanthogenate	green
Captax	bluish green
Vulcacit P (and other addition products of secondary amines and carbon disulfide)	yellowish green

Dr. W. L. Haase, Berlin-Dahlem, examined the colors. Compared with the Ostwald color atlas, they are as follows:

Diphenylguanidine	la 12
O-tolylguanidine	ca 7
Zinc o-butylxanthogenate	lc 24
Vulcacit P	pg 24
Captax	le 22

The values are based on a layer 1 cm. thick, indirectly lighted from below by diffuse light after a maximum depth of color was reached.

7. The last assumption is confirmed by the experiments of Scholtz (*Kautschuk,* **1927,** 101): Some accelerators (such as hexa) in the presence of zinc oxide are capable of lowering the melting

point of sulfur, while others (such as Captax) require the addition of oleic acid besides. The latter fact may be explained by the fact that in the absence of oleic acid zinc oxide reacts with Captax to form a salt; if, however, oleic acid is present, zinc oleate may be formed, and the Captax can enter the salt complex as a neutral constituent.

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Chemical Reactions in Rubber Compounds

I. Reactions between Pine Tar and Litharge

W. H. Reece

When the rubber technologist introduces into his stock substances which will react chemically, he generally does so in order to produce some advantageous modification of the vulcanization process. The published work dealing with chemical reactions involved between rubber, sulfur, accelerator, zinc oxide, and fatty acids is large, but less attention has been given to the study of other chemical reactions which may take place in a rubber compound either before or during vulcanization and in which the vulcanization process itself plays no part.

When the vulcanization of a rubber compound is accelerated by litharge, lead sulfide is produced. Lead sulfide is one of the end products of a chemical reaction or possibly a series of chemical reactions in which rubber, litharge, sulfur, and the fatty acids naturally present in the rubber take part. As vulcanization is accelerated, it is an example of the type of chemical reaction first mentioned. If, however, the sodium salt of a peracid such as sodium perborate be also added, the black lead sulfide is oxidized to white lead sulfate and a white product obtained (G. Bernstein, French patent 536,733 (1921); see *India Rubber J.*, **64**, 261 (1922)). This is an example of the second type of chemical reaction, as it is not connected with the actual vulcanization process. This paper deals with chemical reactions of this latter type which occur in a rubber compound when both litharge and pine tar are present together.

As the composition of pine tar may vary considerably from one sample to another, a sufficiently large quantity for the experimental work was selected from a work's delivery. It was a medium grade tar and had a specific gravity of 1.070.

Pine tar is of an acidic nature and it is, therefore, only to be expected that it will react chemically with oxides to form soaps. For example, when an excess of litharge is added to pine tar, a considerable amount of heat is liberated and after a short time the mixture becomes quite stiff. A hard, brittle mass is finally obtained, but unless external heat is applied, the process takes several hours. This brittle mass softens considerably when heated but regains its former state on cooling. Similar results are obtained if other basic substances are added to pine tar; the reaction with lime, for example, is quite vigorous and the resulting product very hard. A somewhat similar change occurs when rosin is hardened for varnish manufacture by means of the addition of lime. Zinc oxide or magnesia also react with pine tar but the reaction is rather slow and very little stiffening takes place; however, it is considered that these latter reactions are probably different from those obtained by the addition of either litharge or lime to pine tar.

That a reaction takes place in a rubber compound when litharge and pine tar are present together is shown by the appreciable hardening which occurs shortly after litharge is added to a pine tar and rubber mixture. The following plasticity determinations illustrate this effect:

Mixing	A	B
Rubber—parts by weight	100	100
Pine tar—parts by weight	15	15
Litharge—parts by weight	...	15
Plasticity	2.3 secs.	11 secs.

In these experiments the rubber for both mixings was masticated excessively on cold laboratory rollers. The pine tar was then added after thorough mixing, and the resultant mass divided into two equal portions. One of the portions was set aside to represent mixing A. To the other portion the necessary amount of litharge was added as quickly as possible in order to produce mixing B. The plasticity determinations were carried out on both samples 24 hours later, the temperature of extrusion being 85° C.

The hardening may also be observed by heating samples of the two rubbers, A and B, in an oven. The mixing containing litharge did not appreciably alter its shape at 70° C., but the other mixing was rendered sufficiently fluid to spread itself over the supporting surface.

Samples of these mixings were extracted with acetone after heating for 24 hours in the oven at 70° C. The results obtained were: mixing A, 15.81%; mixing B, 9.11%.

As mixing A contained 13.04 per cent of pine tar, the rubber resin present in the extract was 2.77 per cent. This represented 3.19 per cent of the actual rubber. If a similar constitution be assumed for mixing B, the extract will be made up of 2.45 per cent rubber resin and 6.66 per cent of pine tar. Hence, 42.3 per cent of the pine tar had combined with the litharge. This calculation does not take into account any reaction which occurred between the litharge and the acids present in the rubber resins.

Unless vulcanization in a mould is adopted, mixings in which the two ingredients are present often give porous products on account of the water developed during the reaction. It is difficult to measure accurately the amount of water evolved, but the following experiment was carried out in order to determine whether the result agreed approximately with that of experiments described later in which the two ingredients were directly heated together. The compound selected was made up as follows: rubber, 200 g.; sulfur, 6 g.; litharge, 30 g.; and pine tar, 30 g. All the ingredients, with the exception of the pine tar, were thoroughly dried before use. The compound was made on cold laboratory rollers, sheeted out as thinly as possible, and then placed immediately in a cylindrical vessel through which a stream of dry carbon dioxide was passed. The stream of carbon dioxide removed from the rubber any water formed during the vulcanization process. After leaving the cylindrical vessel, the carbon dioxide passed through a cooled, weighed U-tube, where most of the moisture in the gas was condensed, and subsequently dried by passing through weighed calcium chloride tubes. Air was removed from the apparatus by means of the current of dry carbon dioxide, and then vulcanization was effected by heating the cylindrical vessel in an oil bath heated to 140° C. The stream of carbon dioxide was also heated to this temperature before entering the vessel in which the vulcanization took place. The amount of water evolved was obtained from the increase in weight of the receiving apparatus. The moisture (1.31 g.) was slightly in excess of the theoretical result (1.17 g.) calculated from experiments made in the absence of rubber, possibly on account of the additional reaction between the excess of litharge and the rubber resins.

Attention was then directed to the reaction between pine tar and litharge in the absence of rubber. Measurement of the water evolved appeared to be the most simple way of estimating the extent of the reaction, but as pine tar generally contains some free water, a suitable method for its estimation had first to be investigated.

Estimation of Free Water in Pine Tar

As the pine tar boiled at a higher temperature than 100° C., the preliminary experiments were carried out by distilling off about 10 per cent of the pine tar and

measuring directly the water present in the distillate, which separated into a heavy aqueous layer and a lighter layer of oil. Such a method, however, involved heating the pine tar to temperatures of 350–400° C. and it was thought that some change in the pine tar might take place at this temperature which would make the results inaccurate. The experiment was, therefore, repeated after adding petroleum ether to reduce the temperature of distillation. The amount of water obtained was very much lower than before and thus indicated that probably some reaction had taken place at the higher temperature. The method finally adopted was found to be a modification of that described in pamphlet D. 95–28 of the American Society for Testing Materials. A measured amount of pine tar (about 100 g.) was mixed with 100 cc. of petroleum ether and the mixture boiled in a 500-cc. round-bottom flask to which a reflux condenser was attached by means of a trap. The condensed liquid, consisting of petroleum ether and water, was discharged from the condenser into the trap. The lighter petroleum ether overflowed from the top of the trap and returned to the flask, while the heavier water sank to the bottom of a limb graduated to read in multiples of 0.1 cc. and where its volume could be read off directly.

The petroleum ether used had a boiling point range of 140–180° C. A solvent of this initial boiling point was selected in order to carry out the reaction under temperature conditions comparable with those of vulcanization. Subsequent experiments indicated that this precaution was unnecessary and that the operation could be more conveniently performed with a solvent having a lower initial boiling point. A solvent, similar to that recommended by the American Society for Testing Materials, is probably as good as any. This specification requires a small percentage of the solvent to boil just below 100° C. With a solvent of this nature it is easier to remove the film of moisture which collects in the condenser tube above the point of condensation of the solvent.

That the refinement of carrying out the experiment at 140° C. was unnecessary was shown by a further experiment in which the moisture was estimated by passing a stream of dry air through a solution of pine tar in benzene at ordinary temperatures and subsequently passing the air through weighed calcium chloride tubes until no further increase in weight of the latter was obtained. This took about 24 hours. The result agreed very closely with that obtained at 140° C.

Method	Water present %
Distillation with petroleum ether at 140° C.	1.4
Estimated at ordinary temperatures	1.3
Direct distillation	3.4

Estimation of Water from the Chemical Reaction

After the estimation of the free water in the pine tar, the apparatus was cooled down to laboratory temperatures and an excess of litharge added to the mixture. Refluxing was then continued, heat being supplied by immersing the flask in an oil bath. On the completion of the operation, the amount of additional water liberated was read off from the graduated limb. The weight of water liberated with 100 g. of dry pine tar was 2.5 g.

Estimation of Lead Soluble in Pine Tar

The extent of the reaction was also measured by estimating the amount of litharge which had reacted with a definite quantity of pine tar.

The method adopted made use of the fact that freshly prepared lead soaps made from resin acids are soluble in many solvents, of which benzene and gasoline are examples. When small amounts of gasoline are added to pine tar, the two

liquids are completely miscible (except for a small amount of carbonaceous matter present in the pine tar). If a larger quantity of gasoline is added, however, a small quantity of thick tar is precipitated which adheres to the sides of the containing vessel. Benzene acts in a similar way but a larger amount can be added before the insoluble tar separates. This solvent was therefore selected. Approximately 10 g. of pine tar were diluted with 50 cc. of benzene and 10 g. of litharge added. This was refluxed on a water bath for 24 hours and then filtered. The filtrate was evaporated to dryness in a beaker and, when all the benzene had evaporated, the remainder of the organic matter was destroyed by boiling with nitric acid. Lead was estimated in the residue. From the result obtained for the amount of lead soluble in the pine tar, the quantity of water liberated from the reaction between litharge and pine tar was calculated on the assumption that the reaction was a simple one between the litharge and pine tar acids. The weight of litharge which reacted with 100 g. of pine tar was 30.37 g. and the equivalent amount of water was thus 2.45 g. Further experiment showed that reduction of the litharge to metallic lead took place.

Resin Acids in Pine Tar

As the resin acids present in pine tar are volatile, direct estimations were found to give very variable results. This method was therefore discarded in favor of an indirect method in which the percentage of acids present was obtained by difference. Experiment showed that at a temperature of 70° C. the acidic portion of pine tar is ten to twenty times more volatile than the neutral components.

The following method was used for the estimation of the non-acidic components or neutral oils present in pine tar. A weighed amount of pine tar was shaken with excess of 0.5 *N* caustic soda solution. The neutral oils were extracted from the emulsion by means of methylated ether in which pine tar, with the exception of the small amount of solid suspended carbonaceous matter, is completely soluble. The ether extract was filtered, the ether removed by distillation, and the residue weighed. This represented the neutral oils present in the pine tar.

The acids were considered to be that fraction not accounted for by neutral oils, carbonaceous matter and water.

With the pine tar selected, the following analysis was obtained: neutral oils, 50.9 per cent; moisture, 1.4 per cent; carbonaceous matter, 0.8 per cent; acids (by difference), 46.9 per cent. The amount of acid agrees as closely as can be expected with the amount (42.3 per cent) of pine tar which combined with litharge in the rubber mixing mentioned earlier.

Summary

The results of the experiments indicate that when litharge and pine tar are present in a rubber mixing, a chemical reaction takes place which does not appear to differ from that which occurs between litharge and pine tar in the absence of rubber. The figures obtained are also in agreement with the assumption that the reaction is one in which the acids present in the pine tar react with the litharge to form soaps.

It has been shown that the pine tar contained 46.9 per cent of acids which reacted with litharge to produce 2.45 per cent of water.

The author wishes to thank the laboratory staff of the Leyland & Birmingham Rubber Co., Ltd., for assistance in the experimental work, and Mr. R. W. Lunn for his interest and advice.

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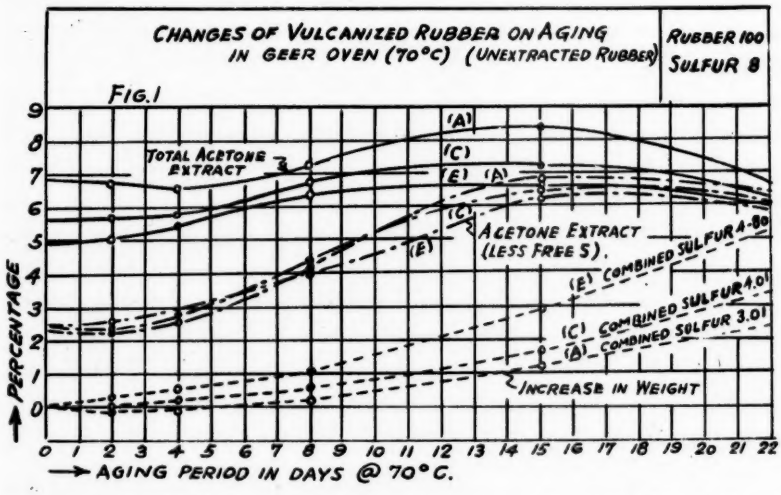
Studies in the Oxidation of Rubber Mixings

W. Cecil Davey

DUNLOP RUBBER CO., KOBE, JAPAN

The rubber airbags used for inflation purposes during the vulcanization of motor covers gradually change during use, and a hard, brittle material forms inside. The bags can, however, be kept in use long after the rubber or, at any rate, the inside rubber, is in an entirely perished condition. The ordinary physical testing methods used for following the changes in rubber are, therefore, not available under conditions where the deterioration is very intense; but the changes can be satisfactorily followed by chemical methods. In the present paper are given briefly some of the results obtained during extensive studies of rubber submitted to prolonged oxidation in a Geer oven at 70° C.

Experimental.—The samples were vulcanized for varying periods, and after vulcanizing were sheeted out thin and placed in small beakers in the Geer oven.

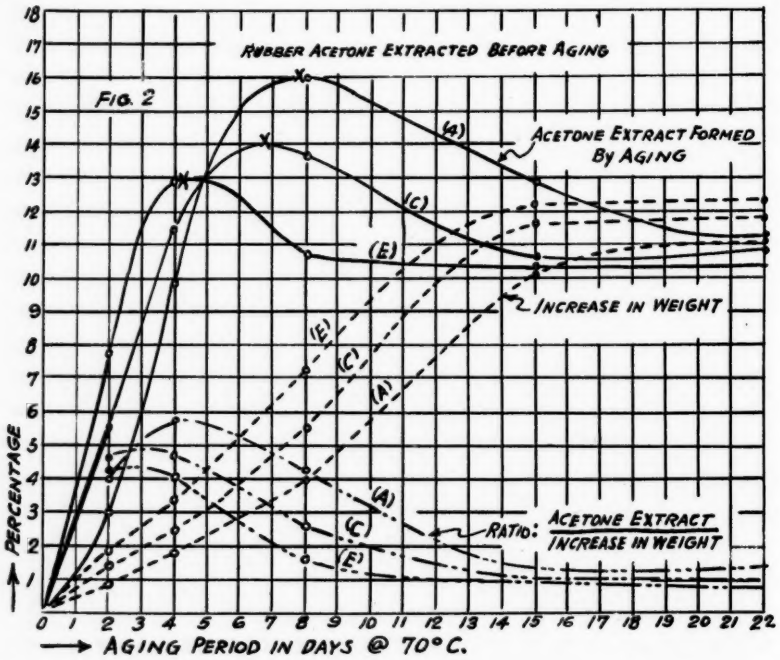


The progress of oxidation was noted from time to time by measuring the increase in weight and by removing and analyzing portions of the samples. In the early experiments rubber-sulfur mixings were used for simplicity, but later the work was extended to accelerated mixings. In order to obtain a theoretical insight into the changes taking place, the rubbers were in some cases extracted with acetone before oxidation (aging); also the aging of rubber previously extracted with first acetone and then chloroform was studied. In some series samples were submitted to repeated aging and extraction, that is, after the extraction following aging the samples were again returned to the oven. After a further period of aging they were again extracted, and so on repeatedly.

Unextracted Rubber.—Figure 1 shows the course of the aging of three samples of differing vulcanization coefficients. It will be seen that the increase in weight

followed the order of the combined sulfur, and no intersection took place. The amount of resinous matter (total acetone-extract less free sulfur) followed the order of the combined sulfur in the early stages of aging, but later the least vulcanized sample had the highest figure. The curves show that at first the production of acetone-soluble matter was very slow, then quite rapid, and afterwards again slow (and a slight decrease might take place).

Acetone-Extracted Rubber.—Figure 2 shows the course of the changes on aging acetone-extracted rubber of differing vulcanization coefficients. The samples were the same as those used for Fig. 1. The oxidation took place very rapidly, and the formation of the acetone-extractable matter increased to a maximum and then decreased to a figure which remained practically constant over a considerable period. In the early stages the most vulcanized sample gave the highest



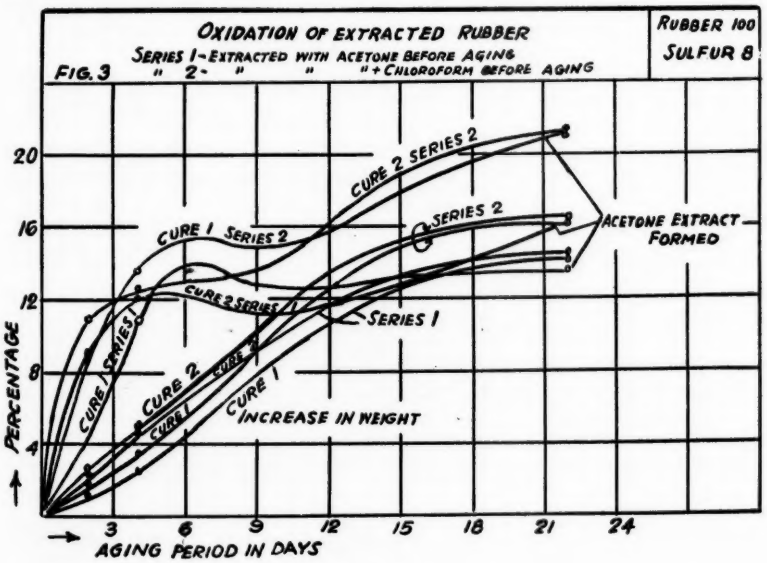
extract, but when the aging was further prolonged the least vulcanized sample overtook the others and yielded the highest extract. Hence the higher the vulcanization coefficient of the original sample, the lower was the figure reached for maximum formation of acetone extract. For the same increase in weight the highest vulcanized sample gave the lowest acetone extract. The increase in weight always followed the order of the vulcanization coefficients and no intersection of the curves occurred. It was subsequently found that if the oxidation was further prolonged the amount of acetone-soluble matter again started definitely to increase. An example of this is seen in Fig. 3.

Chloroform-Extracted Rubber.—When the rubber before aging was extracted with first acetone and then chloroform it oxidized still more rapidly (Fig. 3). The increase in weight and the amount of acetone-soluble matter was higher throughout than that of the corresponding sample extracted with acetone only. After a rapid

formation of acetone-extractable matter there was a slowing up, followed later by a large increase.

Samples Repeatedly Aged and Extracted.—A sample repeatedly aged and extracted with both acetone and chloroform after each stage of aging gave a more oxidized final insoluble residue than a corresponding one extracted after each aging period with acetone only, *e. g.*, one sample (coefficient of vulcanization, 5.25) extracted with acetone only after each aging period gave, after nine agings (and extractions) spread over 43 days, an almost black residue containing 19.15 per cent oxygen; but, when an extraction with first acetone and then chloroform was made at each stage, the black residue contained 25.41 per cent oxygen. In the early stages of oxidation the sample with the highest vulcanization coefficient yielded the highest acetone extract, but in later stages this order was reversed.

Further Aging of the Acetone Extracts.—The acetone extracts formed on aging can be largely converted to an insoluble form on further heating at 70° C. The

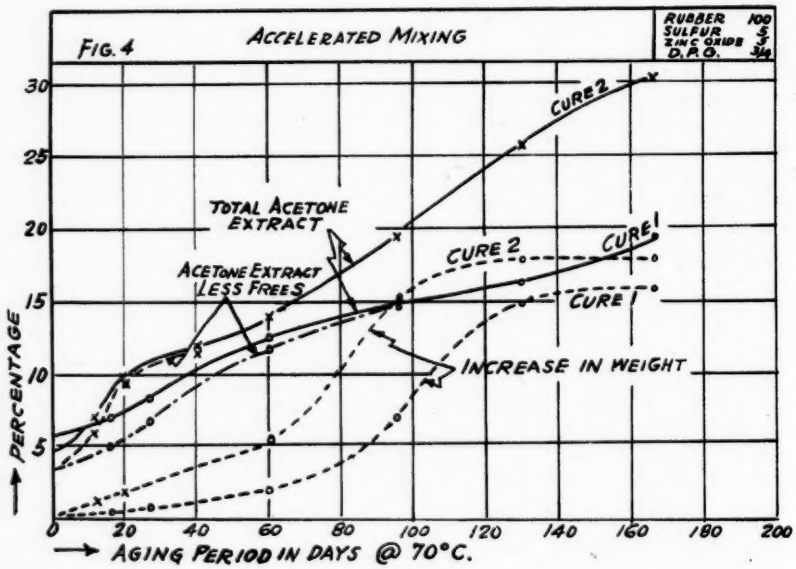


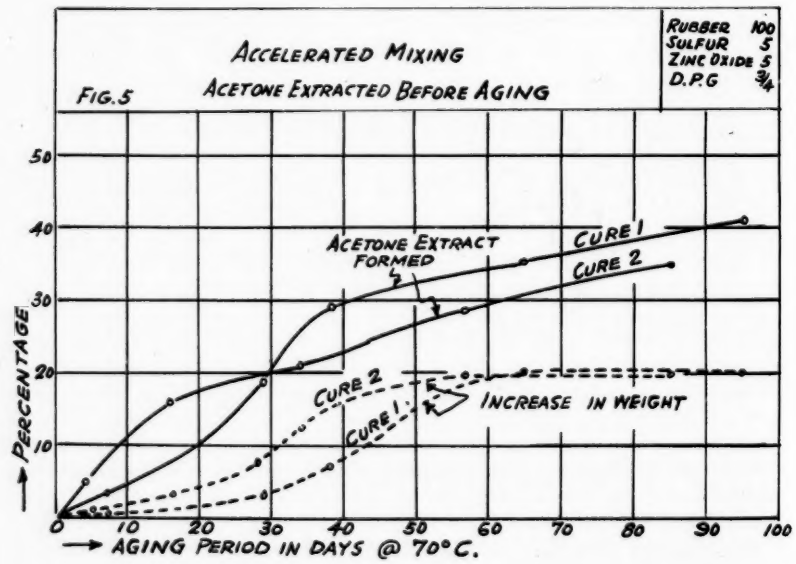
heating also brings about an increase in weight, the percentage depending on the stage of aging from which the sample was obtained, *e. g.*, an extract formed from a sample aged three days increased about 7 to 8 per cent on further aging, but one from a sample aged about ten days increased from 1 to $1^1/_2$ per cent.

Oxidation of Chloroform-Soluble Matter.—Vulcanized rubber always gives a small amount of chloroform-soluble matter on extraction; the amount depends on the extent of cure, being about 1 per cent with a well-cured rubber. This chloroform extract (rubber of a lower degree of polymerization) can itself be oxidized on heating at 70° C. An increase in weight of 15-20 per cent was obtainable, and most of the resultant oxidized product was insoluble in ordinary solvents. From analyses it was thought that the oxidation products from ordinary vulcanized rubber and from the chloroform-soluble part of it were chemically similar.

Accelerated Mixings.—Figures 4 and 5 show curves for a mixing containing an accelerator. With Cure 1 the sample was slightly undercured, but with Cure 2 (see figs.) the sample was fully cured. The accelerated mixing oxidized much

slower than the rubber-sulfur mixing but eventually caused a higher increase in weight. It tended to produce more acetone-soluble matter than the rubber-sulfur mixing.





Conclusions.—All the curves show that there are three stages in the oxidation of rubber; first, when oxidation is slight and the oxygen absorbed yields acetone-soluble matter. Then a stage is reached when the increase in weight is much more

rapid than the production of soluble matter; and, finally, a stage when the acetone-soluble matter tends to increase while the oxygen absorption meanwhile remains constant. It is concluded that the change of acetone-soluble matter to insoluble matter is a reversible one.

The third stage of aging when depolymerization of the insoluble matter takes place is not likely to be reached in practice, *e. g.*, in airbags. The most important stage is the second, when the resinous matter polymerizes to insoluble matter, this latter material causing brittleness. Hence the longer this stage of aging, when oxygen absorption takes place with formation of insoluble matter can be delayed, the longer can the rubber airbag be retained in use.

As a result of the experiments briefly mentioned it is believed that the main outline of the aging of rubber in a Geer oven may be represented on the following basis:

Vulcanized Rubber	$\rightleftharpoons$	Rubber in a lower state of polmerization (chloroform-soluble)	$\rightleftharpoons$	Resinous matter (acetone-soluble)	$\rightleftharpoons$	Oxidized matter (insoluble)
A	$\rightleftharpoons$	B	$\rightleftharpoons$	C	$\rightleftharpoons$	D

The higher the vulcanization coefficient the greater the tendency for the reaction to proceed from A to D and the greater the instability throughout. Extraction with acetone increases the tendency to oxidation, and additional extraction with chloroform will further increase this tendency. On the other hand, the presence of a considerable amount of oxidized matter will tend to prevent further oxidation.

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Colloid Chemical Changes in Rubber and Fatty Oils

László Auer

In attempting to solve many of the problems in connection with the chemistry of rubber and of the fatty oils, it is usually found necessary to employ the main principles of colloid chemistry. It is, however, impossible definitely to classify rubber, as either lyophobic or lyophilic in nature. Raw rubber, such as pale crepe or smoked sheet, is in the presence of organic solvents of lyophilic nature, whereas it is entirely lyophobic when dispersed in water. Rubber latex shows an intermediate behavior between lyophobic and lyophilic systems. After neutralization of the electrical charge of the particles, *i. e.*, at the so-called isoelectric point and slightly beyond it, the rubber particles do not flocculate. From this behavior it may be imagined that latex is a lyophilic system, but it is found that a comparatively small excess of electrolyte causes complete flocculation of the rubber, *i. e.*, the salting-out of the rubber particles. Freundlich and Hauser (*Kolloid Z.*, **1925,** Erg. Bd. 36) have shown that the rubber particles in latex are made up of a liquid interior and a semi-solid external layer. The protein and resin content of the latex are supposed to be present in this external layer of the particles. Von Weimarn (*Bull. Chem. Soc. Japan*, **3,** 157 (1928)) has found that if latex is treated with solvents or solutions which are dispergators (dispersing agents) of protein compounds, and which thus cause a dispersion of the proteins from the external layer of the particles, the emulsion of the rubber hydrocarbon, normally lyophobic in character, will immediately assume a lyophilic nature and the whole system will gelatinize to a solid mass. It seems to be probable that in latex the rubber hydrocarbon is in a lyophilic state and that the partly lyophobic nature of latex is due to the lyophobic character of the protecting protein layer. Immediately this is dispersed, the lyophilic nature of the rubber hydrocarbon becomes evident. Concentrated lithium iodide solution acts as a suitable protein dispergator. As proteins have partly lyophobic and partly lyophilic nature, it is possible that the protein itself forms a gel skeleton containing the rubber hydrocarbon particles dispersed in it. In this case the rubber hydrocarbon may be of a lyophobic nature. Against this hypothesis is the fact that the gelatinization occurs in the presence of protein dispergators and not in the presence of protein coagulators.

The rubber hydrocarbon in the latex is, to a large extent, in a liquid state, but after coagulation by means of electrolytes or air, it is in an apparently solid state. Stamberger supposes that the coagulators act on the rubber hydrocarbon in the latex as polymerizing agents, but the author prefers to regard the change as an aggregation.

The terminology of aggregation and disaggregation was put forward by Harries and Nagel (*Ber.*, **56,** 1048 (1923)) from a consideration of the properties of shellac resin. This resin is composed of two different solid phases existing in different physical states, but having similar chemical constitutions. The two phases form a special type of colloidal system termed isocolloidal. Such a system may exist either in a solid jelly-like "gel" state or in a liquid "sol" state. The change sol to gel, *viz.*, gelatinization, is supposed to be a type of coagulation, which in the case of isocolloids may be accompanied by a change in the concentration of the disperse phase. Aggregation is also a type of coagulation in which the sol-gel

change does not necessarily occur. In other words, a liquid isocolloidal system may be aggregated and yet remain liquid and a solid isocolloidal system may also be aggregated. In the case of aggregation, the degree of dispersion decreases and the particles coalesce to form coarser particles. Aggregated products show small chemical activity and solubility, and differ from chemically polymerized products in that they may be peptized to an increased degree of dispersion by simple treatment with dispersing agents; whereas chemical polymers are not depolymerized by such treatment. Ordinary shellac resin may be aggregated with ether containing hydrochloric acid, and this aggregated product may be peptized with the aid of fatty acids of low molecular weight, *e. g.*, formic acid.

The best examples illustrating the difference between a polymerized product and an aggregated product are distyrene and metastyrene. (Stobbe and Posnjak, *Ann.*, **371,** 259, 287 (1909–10).) Distyrene is formed by treatment of styrene with hydrochloric acid at high temperatures, and is a liquid product having the properties of a definite chemical compound. It distils unchanged (b. p. 312° C.), adds two atoms of bromine giving a bromide with a definite melting point, and cannot be separated by physical methods into two or more different phases. It is a polymer of styrene. When acted upon by light or heat, however, styrene forms solid products having consistencies ranging between jelly-like and glass-like. These products, when dissolved in benzene and then precipitated with alcohol, yield a white powdery product called metastyrene, which does not show any lowering of melting point or raising of boiling point when dissolved in solvents, and has not the properties of a definite chemical compound. In the opinion of the author, metastyrene is the most typical example of an aggregated product. Metastyrene powder forms the disperse phase in the isocolloidal system of the jelly-like solidified styrene, the hardness of which depends on the concentration of powdery metastyrene in the system. With increasing concentration of metastyrene the jelly becomes harder and harder, and the melting point increases. Stobbe and Posnjak also found that metastyrene with various organic solvents forms jellies similar to those which it forms with unchanged liquid styrene, showing that an isocolloidal system, for instance, stryene-metastyrene, is quite similar to a colloidal system benzene-metastyrene. Thus, it is evident that hard, glass-like jellies may be built up from and contain liquid components and constitute a two-phase system.

Metastyrene jelly at higher temperatures is similar to rubber at room temperature (cf. Staudinger, *Ber.*, **59,** 3036 (1926)); Hünemörder (*Kautschuk*, **1927,** 106). The fact that rubber is built up of two different phases of the same hydrocarbon has been demonstrated by several workers, especially by Pummerer and collaborators (*Ber.*, **60,** 2148 (1927); and **61,** 1583 (1928)), who have been able to separate a very pure rubber hydrocarbon into two phases. For convenience these two phases will be referred to as α- and β-rubbers. The so-called α-rubber is ether-soluble and shows a lower melting point than the so-called total rubber of Pummerer. (Total rubber is the name for the purified resin- and protein-free rubber hydrocarbon.) Pummerer has found 55 to 80 per cent of α-rubber in the total rubber and 20 to 45 per cent of β-rubber, which is insoluble in ether. The raw rubber should be considered as a jelly. The β-rubber seems to be the gel skeleton in the jelly system of rubber, whereas the α-rubber seems to be the dispersion medium in the jelly. In other words, the β-rubber should be a similar product to metastyrene, whereas α-rubber should be similar to the liquid styrene. In the author's opinion the β-rubber seems only to be a more concentrated solution of the disperse phase itself. The α-rubber, on the other hand, is more concentrated with respect to the dispersion medium of the rubber jelly than β-rubber, but it

is not the dispersion medium itself. Owing to the fact that Pummerer could not find a better separating agent for the rubber jelly than ether, it is probable that by this method he only succeeded in concentrating one of the two phases of the jelly and not in isolating the pure phase.

It should be mentioned at this point that the results of the recent X-ray researches on the structure of rubber are in agreement with the above two-phase theory of the structure of rubber (Bary and Hauser, *Kautschuk*, **4,** 96 (1928)). The X-ray diagrams of frozen rubber show that the β-rubber increases its concentration at the expense of the α-rubber. In the case of the stretching of normal rubber, the α-rubber particles are squeezed out from the gel skeleton built up by the β-rubber. The β-rubber seems to form a type of space lattice which can be seen, either when the concentration of the β-rubber is high enough, or through orientation of itself during stretching into parallel fibers. The X-ray investigations have also shown that the elementary particle of the rubber hydrocarbon is built up by the union of eight isoprene molecules, and molecular weight determinations (cf. Pummerer, *loc. cit.*) on the α-rubber have approximately confirmed this fact. Rubber may be visualized as being built up of different aggregated forms of such elementary particles, but it should be kept clearly in mind that, while the elementary particle is a polymerized isoprene product, the elementary particle itself does not polymerize further in the strictly chemical sense of the word. The disaggregating action of organic solvents on rubber explains the different molecular weights of the same rubber sample in different solvents. These different molecular weights show that the various solvents disaggregate the raw rubber to different extents.

The fact that the coagulating agents aggregate the rubber and that the rubber solvents act as disaggregating agents is supported by a recent unpublished observation of Stamberger, who found that when organic solvents, *i. e.*, ether or carbon tetrachloride, which act as swelling agents on raw rubber, are added to the latex and the water and the solvents are then allowed to evaporate, the remaining rubber film has not a solid nature as usual, but it is a very sticky, pasty product. After a few days the rubber film loses its stickiness and shows the usual appearance of rubber film produced from latex by simply evaporating off the water. In the author's opinion, the disaggregating agents in this case retard the aggregation caused by the air.

Changes observed in the case of styrene have been used as analogies, in many cases, in studying changes in fatty oils. The chief theory of the drying of fatty oils was based, until very recently, on the observation that fatty oils adsorb oxygen from the air if they are exposed in thin films. It was supposed that the fatty acids of the fatty oils were oxidized during the drying process, and that such oxidized fatty oils built up the gel skeleton in the jelly of the dried oil films. It was observed recently by the author that fatty oils dried in atmospheres of inert gases, and that a drying process also occurred in desiccators which were evacuated with the aid of a water pump. Further experiments showed that in a very high vacuum obtained by means of a mercury vapor pump no drying process took place. The experimental data of these investigations were explained by the gas coagulation theory of the drying process (*Kolloid-Z.*, **40,** 334 (1926); *Chem. Umschau Fette, Oele, Wachse, Harze*, **33,** 216 (1926); **35,** 9 (1928); *Farben-Ztg.*, **32,** 30 (1927)). It was supposed that the fatty oils were isocolloidal systems in which the dispersed phase and the dispersion medium were formed from the same chemical compounds similar to styrene and to rubber. In the isocolloidal fatty oil system the disperse phase may increase its concentration at the expense of the dispersion medium in four different ways: (1) by the action of ultra-violet and X-rays; (2) by the action of heat; (3) by the action of certain aggregators such as electrolytes, electrolyte

solutions, or organic solvents; (4) by the action of gases, for instance, by the action of oxygen.

To prove the above hypothesis, experiments were carried out to find a reagent which would act as coagulator on the isocolloidal system of the fatty oils. It was expected that such a coagulator would separate the system into two phases: into the coagulated disperse phase and the dispersion medium. Such a coagulator for the isocolloidal system of jelly-like styrene in benzene was found in alcohol. The author succeeded in finding a similar coagulator for the fatty oil systems in formic acid (*Kolloid-Z.*, **42**, 288 (1927)). If linseed oil is shaken with an equal volume of formic acid and allowed to stand the system separates into two distinct layers. The top portion is the fatty oil dispersion medium, the bottom portion consists of formic acid, and at the boundary of these two distinct layers a very slight precipitation of the disperse phase is to be observed. Formic acid under these conditions is only a moderately good coagulator, and therefore in the case of certain fatty oils the amount of coagulated disperse phase is so small as to be barely noticeable. When formic acid is shaken with a boiled linseed oil containing cobalt linoleate as dryer, and the liquid allowed to separate, three distinct layers can be seen. The middle layer contains precipitated cobalt linoleate as well as an amount of dispersed phase of linseed oil. The boiling has increased the concentration of the disperse phase and for this reason a larger amount of disperse phase is obtained in the middle layer. The cobalt linoleate has the action of a sensitizer which catalytically assists the increase in concentration of the disperse phase and also accelerates the flocculation of the disperse phase after the formic acid is added. When comparing the drying velocities of the original linseed oil with those of the boiled linseed oil and of the disperse phase of the linseed oil after the formic acid flocculation, it is found that the dispersion medium of the boiled linseed oil dries not only slower than the boiled linseed oil, but also much slower than the original linseed oil. This shows that the dispersion medium of the flocculated boiled linseed oil can dry only after the air has caused the formation of a new disperse phase. The separated disperse phase of the boiled linseed oil is able to form films not only with the original dispersion medium part of the fatty oil, but also with mineral oils and other dispersion mediums which would not form a film without the presence of such a gel skeleton. Experiments have been carried out with thickened oils, such as blown oils and stand oils, and it was found that in all cases the concentration of the disperse phase is enormously increased above that of the original oil. When a boiled stand oil is further boiled with the addition of driers it can be observed that the drier causes a further increase in the concentration of the disperse phase and that it accelerates the flocculation. Similar observations were made on so-called uviol-oils which were thickened with the aid of ultra-violet rays.

The formic acid flocculation shows, firstly, that the increased viscosity of thickened oils is due to the increased concentration of the disperse phase; secondly, that such concentration increase may be caused equally well by blowing, heating, and irradiation with ultra-violet rays; and thirdly, that for the gelatinization of fatty oils either in the case of film formation in the drying process or in the jelly formation during bodying a certain concentration of dispersed phase is necessary. This disperse phase acts as gel skeleton in the formation of the jelly.

Of the many possible ways of increasing the disperse phase concentration, the one in which oxygen is the cause of such process is the most interesting. Fatty oils as well as rubber and styrene contain unsaturated carbon compounds and may add oxygen or ozone either with removal of unsaturation and, or, the formation of smaller molecules. It has been proved in many interesting ways that

oxygen decomposes fatty oils giving definite fission products, but there is no proof up to date that either in the film formation (of fatty oils), or in the bodying of fatty oils, the chemical action of oxygen is essential. In the vacuum desiccators in which the author observed a drying process, the oxygen concentration present was not enough to form any chemical compound. It was, therefore, supposed that gases generally have a coagulating action upon lyophilic colloidal systems similar to that of small concentrations of electrolytes upon lyophobic colloidal solutions. Just as, in order to coagulate the latter, a minimum concentration (threshold value) of coagulating electrolyte is necessary, so a threshold value of gas ions is necessary for gas coagulation to occur. Also just as ions of the coagulating electrolyte may be adsorbed by the coagulum, so gaseous ions may be adsorbed during the gas coagulation of lyophilic systems such as drying oils. Adsorbed gases generally are very active, and this may explain why oxidation occurs during film formation of linseed oil, for instance, under normal atmospheric conditions. In the case of a gas coagulation such a chemical reaction is not absolutely essential, but it may accompany the primary reaction. If gases, other than oxygen, act as coagulators the action differs from that of oxygen only in degree.

That gases have a physical action on rubber has not been fully realized. The film formation on the latex-air boundary is similar in appearance to that which occurs at a protein hydrosol-air boundary. Besides proteins, boiled fatty oils, certain metal sols prepared according to Paal, certain dyestuff sols, and also mercury and amalgams show the phenomenon of film formation at the liquid-gas boundary. The above products are partly colloidal solutions and partly isocolloidal systems. Mercury is one of the isocolloidal systems and the film formation occurring at the mercury-air boundary was carefully studied by Schütt (*Ann. Physik*, **4,** 712 (1904)), who demonstrated the role played by oxygen in this phenomenon. He studied the film formation on zinc amalgam under petroleum and under glycerol. He found that at the boundary zinc-amalgam|glycerol no film formation occurred, but at the zinc-amalgam|petroleum boundary a film formation occurred very readily. Schütt analyzed the petroleum and glycerol for oxygen and found that while glycerol was free, the petroleum contained a large amount of dissolved oxygen. He could not find any oxide formation in the film, so it seemed probable that the oxygen acted in a physical rather than in a chemical manner.

The above considerations indicate that the coagulation of latex on exposure to air is due to the coagulating action of oxygen on the colloidal system of latex. In the preparation of para rubber, the latex is subjected to the action of smoke and the gases present in the smoke are one cause of the coagulation and aggregation of the latex. The smoking process during the manufacture of smoked sheets could be mentioned as a further example of gas action. The rubber jelly has a smaller adsorption power towards the coagulating gases than the jelly of the fatty oil films, hence the comparatively better aging property of rubber compared with fatty oil films.

Rubber may be visualized as a jelly consisting of two physically different phases of rubber hydrocarbon. The rubber, according to this theory, has a similar structure to gelatin hydrogel. A 5 per cent gelatin hydrogel changes from a solid jelly into a viscous liquid on mechanical working, *e. g.*, stirring or shaking. The plasticizing and "killing" effect of mastication is something similar to the effect of mechanical working on other jellies. The comparatively high coherence of the rubber particles accounts for the powerful mechanical work necessary for the breakdown of rubber.

In the case of an electrolyte, the *ions* act as coagulators. It is supposed that in the gas coagulation process gaseous ions are acting. Liquids generally con-

tain small quantities of air in solution. Ultra-violet rays ionize gases, and the action of ultra-violet rays on fatty oils may be caused by the ionization of the dissolved oxygen. Most of such dissolved gases are given off by the liquids just below their boiling points. Fatty oils boil at 300–350° C. Just below this temperature (at which bodying occurs) gas evolution may be observed. The gas particles which bubble out of the liquid may be charged electrically by friction against the liquid molecules (ballo-electrical phenomenon), thus causing an alteration in the colloidal structure of the fatty oil system.

While carrying out some experiments on the heat bodying of fatty oils *in vacuo* it was found that comparatively large amounts of acids insoluble in petroleum-ether were formed, whereas only small amounts of these acids existed before heating. The petroleum-ether insoluble fatty acids have been considered to be "oxy acids," but neither hydroxy-, aldehyde-, or keto-groups have definitely been proved to be present in these acids. To avoid any possible oxidation by contact with the atmosphere the experiments were carried out in distillation flasks fitted with a mercury seal. Before heating, the pressure inside the flask was reduced to 50 mm. mercury. After the heating was stopped, the product was allowed to cool *in vacuo*. In all cases petroleum-ether-insoluble acids varying between 12 and 61 per cent of the total acids obtained on hydrolysis were found. From the amount of petroleum-ether-insoluble acids obtained it was clear that these acids could not be formed by oxidation, as oxidation would require a large volume of oxygen. Combustions carried out on the acids insoluble in petroleum-ether showed that no increase in the oxygen content had occurred. The experiments show that the change of the fatty acids from soluble to insoluble is not dependent upon any chemical oxidation, and it is probable that the acids insoluble in petroleum-ether of heat-bodied oil-jellies differ from those of linoxyn only in the percentage of adsorbed oxygen. The details of these experiments will be published very shortly.

Gases have not only a coagulating action on lyophilic isocolloidal systems, but they can also act as peptizing agents. Linoxyn may be changed into a liquid product by the action of gases. The mastication process of rubber can be explained on the basis of the two-phase theory of rubber, but it is very possible that a gas peptization assists the mechanical working. In other words, the mechanical working itself may cause a gas peptization. The jellies contain adsorbed oxygen which may be ionized by friction. Such friction may occur in the case of heating when the gases leave the adsorbing medium or by shaking or stirring the system. During the peptization of a gelatin hydrogel by shaking, a large number of air bubbles are formed throughout the colloidal system. When rubber is masticated, the formation of air bubbles may be observed. These, when destroyed, emit a loud noise. Fry and Porritt (*Trans. Inst. Rubber Ind.*, **3**, 203 (1927)) studied the effect of heat on the lowering of the viscosity of raw rubber and found that in a high vacuum heat does not cause any lowering of the viscosity, whereas in the presence of small quantities of oxygen the viscosity of rubber solutions decreases. Fry and Porritt could not observe any lowering of viscosity in the presence of hydrogen, steam or nitrogen, but Pummerer and Pahl (*Ber.*, **60**, 2152 (1927)) found that the killing of rubber could be effected in an atmosphere of carbon dioxide. The author is of the opinion that gases, other than oxygen, may also cause a peptization, but that the time required for such a process is much longer than in the case of oxygen. Fisher and Gray (*Ind. Eng. Chem.*, **18**, 414 (1926)) found that during the mastication process the iodine-adsorption power of rubber decreases slightly, which they think is due to a small oxygen adsorption during this process. (Regarding the effect of heat on rubber, cf. Park, Carson, and Sebrell, *Ind. Eng. Chem.*, **20**, 478 (1928).)

As sulfur is very similar in its behavior to oxygen, many attempts have been made in the case of both rubber and fatty oils to study vulcanization in comparison with oxidation. (Whitby and Chataway, *J. Soc. Chem. Ind.*, **1926**, 115T.) Sulfur-bodied and oxygen-bodied fatty oils are very similar. Both of them contain petroleum-ether-insoluble acids, and the appearance of the jellies is somewhat similar. According to the gas coagulation theory, only a very small amount of oxygen is required to bring about colloidal changes. The author has proved the same for sulfur, as he has prepared completely vulcanized oils, using only 1½ per cent of sulfur. Sulfur acts on the fatty oils during vulcanization in a manner similar to the action of oxygen during film formation: firstly, it increases the concentration of the dispersed phase in the fatty oils; and, secondly, it coagulates the system containing the increased concentration of disperse phase. It is understood that, in the case of coagulation, the coagulator may be adsorbed in a secondary reaction by the isocolloidal system of the fatty oil. If the sulfur is present in a large enough excess, it is certainly possible that the adsorbed sulfur can subsequently combine chemically with the fatty acids, similarly to the combination of atmospheric oxygen during and after film formation. Just as such a chemical oxidation of the fatty oils is not essential for the drying process (as they form films *in vacuo*), so also the chemical combination between sulfur and fatty oils is not primarily necessary for the vulcanization process.

The vulcanization can be carried out at various temperatures ranging between ordinary room temperature and about 200° C. The concentration of sulfur necessary for the vulcanization varies also over a large range. This fact clearly shows that the vulcanization is something different from an ordinary chemical reaction. The difficulty of accepting a purely physical theory of vulcanization lies in the fact that nobody has yet succeeded in removing quantitatively the combined sulfur from a vulcanized jelly. The explanation of this fact need not be based upon the theory of chemical combination. To remove an adsorbed product from the material in which it is adsorbed is not a simple matter. Such removal can be carried out generally in two ways. In the first case it is necessary to find a substance which is more readily adsorbed by the adsorbing product than the first adsorbed matter. In the case of vulcanized rubber or vulcanized oil it would be necessary to use a reagent which is more readily adsorbed by the isocolloidal system than sulfur, in which case the sulfur could be replaced by the new reagent. The second way to remove the sulfur from the adsorbed material is to find a new adsorbing or dissolving material which has a higher affinity for sulfur than the isocolloidal system of rubber or of fatty oil. In both cases it is essential that the new reagent should come into intimate contact with the adsorbed sulfur particles. But through the sulfur aggregation the isocolloidal systems lose their solubility and chemical activity, and it is obvious that if a highly efficient disaggregating agent is not found the new reagents cannot attack the sulfur particles which are enclosed in the aggregated particles of the isocolloidal system. Under such conditions it is not surprising that according to the reclaiming method of Spence (Pearson, "Crude Rubber," p. 229), by treatment with aniline and aniline-potassium, it is possible to reduce the combined sulfur content of a vulcanized soft rubber by only 90 per cent in one operation, and that of vulcanized hard rubber by only 73 per cent. It should be also mentioned that Harries (*Ber.*, **46**, 733 (1913)) obtained sulfur-free vulcanized rubber by treatment with concentrated hydrochloric acid with the formation of rubber hydrochloride.

It is known that the adsorption power of certain adsorbing systems has a stoichiometrical nature. This fact shows that the maximum limiting value of 32 per cent of combined sulfur cannot only be explained by the formation of a sulfur compound

of rubber hydrocarbon, but it can also be explained by the adsorption power of the rubber becoming saturated at this point. It is not contended that ebonite with 32 per cent sulfur content does not contain a chemically combined sulfur-rubber compound, but it is considered that the evidence for the chemical nature of ebonite as a sulfur compound is not conclusive.

Recently Bacon (*J. Phys. Chem.*, **32,** 801 (1928)) tried to prove the chemical nature of the vulcanization process by showing that simple desulfurization of vulcanized rubber could not be effected by various means, but in his experiments he did not ensure that his desulfurizing reagents would wet the aggregated particles of vulcanized rubber. One of his most interesting experiments is that in which he peptized fractionally different rubber samples containing different small amounts of combined sulfur. He extracted with benzene the different rubber samples containing combined sulfur. In each case he stopped the extraction many times, removed the saturated extract, and replaced it with fresh solvent. In three such benzene fractions, for instance, in the case of a sample containing 0.1 per cent combined sulfur he got approximately the same concentration of sulfur, *i. e.*, approximately 0.1 per cent. This fact is difficult to understand on the basis of the chemical combination theory, as if a chemical compound were formed with a small percentage of the rubber hydrocarbon present, such a vulcanized compound could not be soluble in benzene and the different benzene fractions could not contain the same sulfur percentage as the original sample. Bacon worked also in the presence of accelerators, and he observed that he got a complete vulcanization only in the case in which 0.5 per cent sulfur is at least combined with the rubber. This limit of 0.5 per cent combined sulfur is also confirmed by other authors, and if, therefore, the sulfur really acts as a coagulator in the vulcanization, the threshold value for rubber in the presence of accelerators should be between 0.5 and 1 per cent sulfur, of which amount at least 0.5 per cent sulfur must be adsorbed during the aggregation process.

Recently Fisher and Gray (*Ind. Eng. Chem.*, **20,** 294 (1928)) studied the vulcanization of rubber with polynitro compounds and benzoyl peroxide, and concluded from their results that ordinary vulcanization is an unknown change in the rubber hydrocarbon involving no change in unsaturation, and that the chemical union of sulfur is a secondary reaction producing a further change, which is a change of degree only and not of kind.

According to the present state of experimental investigations regarding the vulcanizing of rubber, only two theories of vulcanization can be regarded as at all satisfactory. The coagulation or aggregation theory, in which the sulfur plays the role of an aggregator and coagulator, has already been described. The second theory is that which has recently been strongly supported by Stevens (*J. Soc. Chem. Ind.*, **1928,** 37T), and according to which the sulfur forms in all cases a definite chemical compound containing 32 per cent of sulfur. In the case in which 0.5 per cent sulfur is found to be combined with the rubber $1^1/_2$ per cent would be the amount of such sulfur-rubber compound formed, which would build the gel skeleton of the vulcanized rubber jelly. As gelatin solutions with very low concentrations may gelatinize to a jelly, in principle this theory may be accepted, but there are data which seem to be partly in contradiction to it, for instance, the above experiments of fractional peptization carried out by Bacon. As the rubber-sulfur compound is insoluble in benzene, the observation that different fractions show similar sulfur content could hardly be explained. The action of accelerators is also one which is difficult to explain according to the above theory. There are many known cases in colloid chemistry in which small amounts of certain sensitizers make possible reactions which could not be carried out without them under

similar conditions. The author considers the action of the accelerator as that of a sensitizer of the coagulator. As these sensitizers remain in the system they may show a specific action and have some influence on the physical properties of the vulcanized rubber jelly.

Twiss (*J. Soc. Chem. Ind.*, **44**, 106T (1925)) is of the opinion that the action of carbon black on rubber mixes is a similar one to that of sulfur. If a satisfactory amount of carbon black is mixed into rubber, the mix, which was plastic on the mill, aggregates during storing in the air to a product which is similar in many ways to vulcanized rubber. It has also been observed that when such carbon black mixes after storage are built up and cured in layers in the press they do not vulcanize to one single piece of rubber, but each layer vulcanizes separately, a thin film formed over the surface of each individual layer during storage having prevented the formation of a compact mass. This phenomenon is also caused by gas coagulation. Modern carbon blacks do not contain occluded gas in sufficient amount to be harmful during the vulcanization, but investigations of Neal and Perrott ("Carbon Black: Its Manufacture, Properties, and Uses," U. S. *Bureau of Mines Bulletin*, **1922,** No. 192) show that they contain 2 to 7 per cent moisture and 5 to 13 per cent volatile matter, including air, carbon dioxide, and carbon monoxide. The carbon black particles on the rubber-air boundary may also adsorb from the air small amounts of oxygen, and it is very probable that this adsorbed gas is the cause of the skin formation and also for the loss in plasticity of such mixes.

A similar phenomenon to the above-mentioned skin formation in the absence of carbon black was found by Defries and Naunton (*Trans. Inst. Rubber Ind.*, **4,** 298 (1928)) to be caused by ultra-violet ray irradiation. This phenomenon is very probably caused by the coagulating action of the air particles which have been ionized by the ultra-violet rays.

The two-phase theory of isocolloidal systems has recently been applied with considerable success to the production of new products. If a weak gelatin hydrosol is divided into three parts and to one is added a small percentage of sodium sulfate, to the second a small percentage of potassium chloride and the third is kept for comparison purposes, it is observed that the sodium sulfate increases the rate of gelatinization of the system as well as the melting point of the jelly formed, as it has a solidifying action. Potassium chloride retards the gelatinization, lowers the melting point of the jelly formed, and shows, therefore, a liquefying action. It has been found by the author (*Kolloid-Z.*, **47,** 38 (1929)) that if suitable different electrolytes are dissolved in fatty oils with the aid of heat, the gelatinization velocity may be increased or decreased. In the case of fatty oils, the measurement of gelatinization velocity is very difficult, and the simplest way is to follow the change in the melting points of the reaction products. It was observed that sodium sulfate, which had a solidifying action on gelatin-water jelly, showed also a solidifying effect on the oils. Potassium chloride, on the contrary, had a liquefying action on gelatin-water jelly, and also liquefied the isocolloidal systems of the oils.

As during the heating process, which is used for dissolving the electrolytes, the raw oil thickens without the presence of any additional material to a thick stand oil, the so-called liquefied products are actually thicker than the original starting material, but the liquefaction can be easily observed if the product is compared with a stand oil obtained by heating under similar conditions in the absence of any electrolyte. The anions as well as the cations have a distinct role in the process. The role of the cations seems, however, to be slightly more important. Comparing the actions of chemically equivalent amounts of different electrolytes having the same anion products with different viscosities result. If the products are arranged in order of their viscosity, the order of the cations is practically the same

as that observed in many other similar tables arranged according to observations on other phenomena of colloid chemistry.

TABLE I

LYOTROPE CATION SERIES

Different carbonates in quantities chemically equivalent to 3 per cent sodium sulfate were dissolved in linseed oil and the viscosities of the products compared by means of an Engler viscosimeter at 145° C.

The viscosities are expressed as the times taken for 50 cc. of the oil products to flow through the viscosimeter.

Li	22′ 28″	>	Na	10′ 45″	>	K	9′ 35″	>	NH_4	4′ 35″	
Al	18′ 51″	>	Ba	16′ 37″	>	Ca	14′ 30″	>	Sr	7′ 35″	>
Fe	6′ 55″	>	Zn	6′ 35″							

50 cc. raw linseed oil under the same conditions—0′ 16″.

If, on the other hand, chemically equivalent amounts of different electrolytes having the same cation are dissolved similar anion series are obtained to those observed in other similar investigations of colloid chemistry.

TABLE II

LYOTROPE ANION SERIES

Conditions as described for Table I, except that in this case the cation is always sodium and the anion is variable.

$(COO)_2''$	18′ 27″	>	S_2O_3''	17′ 35″	>	SO_3''	14′ 50″	>	HCO_3'	12′ 4″	>
CO_3''	10′ 45″	>	SO_4''	9′ 55″	>	NO_2'	9′ 40″	>	BrO_3'	9′ 25″	>
S''	8′ 52″	>	B_4O_7''	8′ 36″	>	NO_3'	7′ 4″	>	CH_3COO'	6′ 45″	>
Cl'	5′ 45″	>	Br'	5′ 25″	>	S_2O_4''	4′ 50″	>	I'	4′ 45″	>
HPO_4''	4′ 40″	>	CN'	3′ 30″	>	CNS'	2′ 51″				

Thus the nature of the chosen electrolyte is one of the most important factors of the reaction. Further factors influencing the reaction are: the concentration of dissolved electrolyte in the final product, the duration of heating, and the state and kind of the gases present in the reaction chamber. It has been found, for instance, that *in vacuo* the results obtained differ from those obtained at ordinary atmospheric pressure, and that under increased pressure different results are again obtained. After reaching a certain maximum the solidifying action changes into a liquefaction process and the viscosity decreases. This action seems to be caused by the gases present in the reaction chamber, and with a further slight addition of electrolyte the liquefaction process can be again changed into a solidification process. The viscosity changes are very probably due to changes in the electrical structure of the material.

Oils solidified by the aid of electrolytes may show viscosities varying between that of vaseline and that of common resin. Also products similar to raw rubber can be obtained by this process. If the applicability of different fatty oils for this process is studied it is found that the different oils give under the same reaction conditions different results. Comparing, for instance, the viscosity of solidified oils containing 5 per cent of sodium bicarbonate the following series in order of decreasing viscosity is obtained: China wood oil > castor oil > linseed oil > rape oil > fish oil > sunflower oil > olive oil.

The capacity of the different oils for solidification is of a varying degree, but if modifying reagents are suitably chosen there may be obtained from any oil, products similar to those which are obtained from a specified oil using a given electrolyte. This means that a product having certain definite properties can be obtained not only from one particular oil, but from any fatty

oil provided the reaction conditions and reagents used are modified to suit the particular oil in question.

It was found that linseed oil could be brought into a form similar to ordinary resin, and for this reason it was supposed that resins must also be jelly-like products which could be treated by the above process. As the resins are fairly hard products their further solidification is not of interest. Some experiments on the liquefaction of resins have been carried out with satisfactory results. To avoid misunderstanding it is necessary to point out that the liquefaction was not carried out in the way of a destructive distillation, but only by simple fusion *in vacuo* with an electrolyte. During the fusion the electrolyte dissolves in the resin and so causes liquefaction. Such a liquefied resin has properties similar to thickened fatty oils; thus, whereas resin alone is brittle in thin films, the liquefied resin forms an oil-like film. The film formation of such a liquefied resin is quite similar to that of a drying oil. The above experiment is an example showing that the physical properties of isocolloidal systems can be modified without profound change in their chemical nature. It shows also that products with quite different chemical constitutions can be brought into physically similar states.

Experiments have also been carried out to prove the physical nature of the solidifying process of fatty oils and to investigate whether any complex formation occurs during the process. A fatty oil, for instance linseed oil, yields on treatment with 10 per cent crystalline sodium sulfide a solid product. If this solidified oil jelly is extracted in a Soxhlet apparatus with water an aqueous emulsion is obtained. On acidification the emulsion is coagulated and the fatty oil separates on the surface. After taking up the fatty oil with ether, washing the ether solution free from mineral acid, and distilling off the ether *in vacuo* the dried residue has a similar appearance to an oil which has been heated in the absence of reagents under the same conditions as those used in the preparation of the solidified oil. This shows that the action of the sodium sulfide is a physical one and that its presence in the jelly is essential for the jelly structure. If the sodium sulfide had only a catalytic action, after washing out the reagent from the jelly, the latter should remain unaltered. The action of the electrolytes on the oil systems is similar to the action of small amounts of molybdenum, vanadium, chromium, and nickel in special steel alloys. The electrolytes are adsorbed by the micellas of the fatty oils, and it has been observed that, for instance, if the washing out of sodium sulfide from the above sample is attempted by simply boiling up the sample with water the oily mass cannot be obtained ash-free. The difficulties met with in attempting to wash out electrolytes from the oil products are similar to those met with when attempts are made to remove sulfur from a vulcanized product. In the case of sodium sulfide, the use of a Soxhlet apparatus ensures success. This success is due to two factors: firstly, the oil product readily emulsified when treated in the Soxhlet apparatus with hot water; and, secondly, the electrolyte (sodium sulfide) is very readily soluble in water.

It has been pointed out that linoxyn, vulcanized fatty oil (factice or rubber substitute) and vulcanized rubber are from a colloid chemical point of view very similar products. They are all non-thermoplastic products. They are not soluble in organic solvents, but swell readily. Ordinary rubber is, on the contrary, a thermoplastic product which becomes softer under the action of heat, and when masticated is soluble in some organic solvents. When rubber is heated *in vacuo* for a long time at about 250° C. it melts to a viscous liquid, which on cooling does not return to its original state. During the whole process the loss in weight is less than 1 per cent and no appreciable chemical decomposition takes place; the rubber probably undergoes a physical disaggregation. Such disaggregated rubber is

similar to viscous heat-bodied stand oils. Experiments were carried out to vulcanize such heat disaggregated rubber under similar conditions to those under which stand oils are vulcanized, and the similarity in appearance of both products is remarkable. Disaggregated rubber and vulcanized rubber have both corresponding types in fatty oil products. Up to now only raw rubber has had no analog in fatty oil products. The new solidified oil products containing electrolytes may be considered to be the result of the first attempts to get oil products similar to raw rubber. Many of the physical properties and also the appearances of such solidified oils have a distinct similarity to those of raw rubber, especially their swelling properties and behavior toward organic solvents. The only distinct difference between these solidified oils and rubber is that in spite of the fact that both are thermoplastic the molten solidified oils return to their original state after cooling, whereas rubber largely loses its remarkable structure when melted. Besides the swelling experiments, some practical experiments in rubber mixes show that the solidified oil products, in the vulcanized form, have much more rubber-like properties than any other known oil product.

New types of rubber substitutes have been prepared by vulcanization of such solidified oils, and Tables III and IV show tensile results and elongations of rubber mixes containing such vulcanized solidified oils compared with mixes containing ordinary vulcanized oils, *i. e.*, rubber substitute.

TABLE III

PROPERTIES OF THE FOUR TYPES OF VULCANIZED SOLIDIFIED OILS IN A ZINC OXIDE MIX

Standard Mix.—Smoked sheet rubber, 50 parts; pale crepe rubber, 50 parts; sulfur, 7 parts; zinc oxide, 15 parts; triphenylguanidine, 1 part; vulcanized solidified oil, 50 parts. Cured at 40 lbs. steam pressure.

Standard Mix without Substitute				*Dark Substitute*							
								9212			
	Breaking Load		Elong.		Breaking Load		Elong.		Breaking Load.		Elong.
Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break	Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break	Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break
				35′	51.3	729	856	35′	134.9	1915	900
45′	159.1	2259	815	45′	72.9	1035	839	45′	157.1	2231	910
				52½′	99.4	1411	826	52½′	166.2	2360	876
60′	182.7	2594	765	60′	87.5	1243	837	60′	177.6	2523	846
								65′	181.6	2578	880
75′	172.0	2442	815	75′	134.0	1903	852	75′	175.6	2494	853

	9117				1925				2935		
	Breaking Load		Elong.		Breaking Load		Elong.		Breaking Load		Elong.
Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break	Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break	Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break
15′	201.0	2854	940	15′	186.4	2646	870				
25′	201.0	2854	873	25′	192.6	2735	843	25′	106.9	1518	800
30′	205.2	2914	836								
35′	203.3	2887	826	35′	200.2	2843	850	35′	150.5	2137	823
45′	207.1	2941	830	45′	192.8	2738	817	45′	171.5	2435	805
				52½′	190.2	2700	793	52½′	173.3	2460	800
60′	175.8	2497	760	60′	176.5	2506	767	60′	175.6	2494	773
								75′	183.9	2611	810

The Nos. 9212, 9117, 1925, and 2935 indicate various types of vulcanized solidified oil products.

The vulcanized solidified oils form excellent compounding ingredients; for example, if they are mixed into batches of rubber, in the relationship of 100 parts of rubber to 50 parts vulcanized solidified oil the products show equal or higher tensile results than corresponding mixes in which the 100 parts of rubber were

not diluted with any oil product. Ordinary vulcanized oil products, on the contrary, considerably decrease the tensile strengths of rubber batches when used in corresponding proportions.

TABLE IV

PROPERTIES OF THE FOUR TYPES OF VULCANIZED SOLIDIFIED OILS IN AN INNER TUBE MIX

Inner Tube Mix.—Rubber, 100 parts; zinc oxide, 5 parts; barytes, 20 parts; diorthotolylguanidine, 0.5 part; sulfur, 2.5 parts; antimony sulfide, 10 parts; vulcanized solidified oil, 50 parts. Cured at 40 lbs. steam pressure.

Standard Mix without Substitute				*Dark Substitute*							
					9212						
	Breaking Load		Elong.		Breaking Load		Elong.		Breaking Load		Elong.
Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break	Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break	Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break
				35′	60.9	865	773	35′	153.1	2174	960
45′	209.8	2980	870	45′	71.8	1020	810	45′	168.3	2390	933
									166.1	2359	916
60′	216.4	3073	860	60′	89.7	1274	813	55′			
	9117				1925				2935		
	Breaking Load		Elong.		Breaking Load		Elong.		Breaking Load		Elong.
Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break	Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break	Cure	Kg./ Sq. Cm.	Lbs./ Sq. In.	at Break
35′	123.4	1752	907	35′	162.6	2309	836	35′	166.3	2361	810
45′	134.0	1903	840	45′	176.2	2502	823	45′	166.3	2361	790
55′	172.4	2447	887	55′	158.8	2256	803	55′	155.1	2203	766

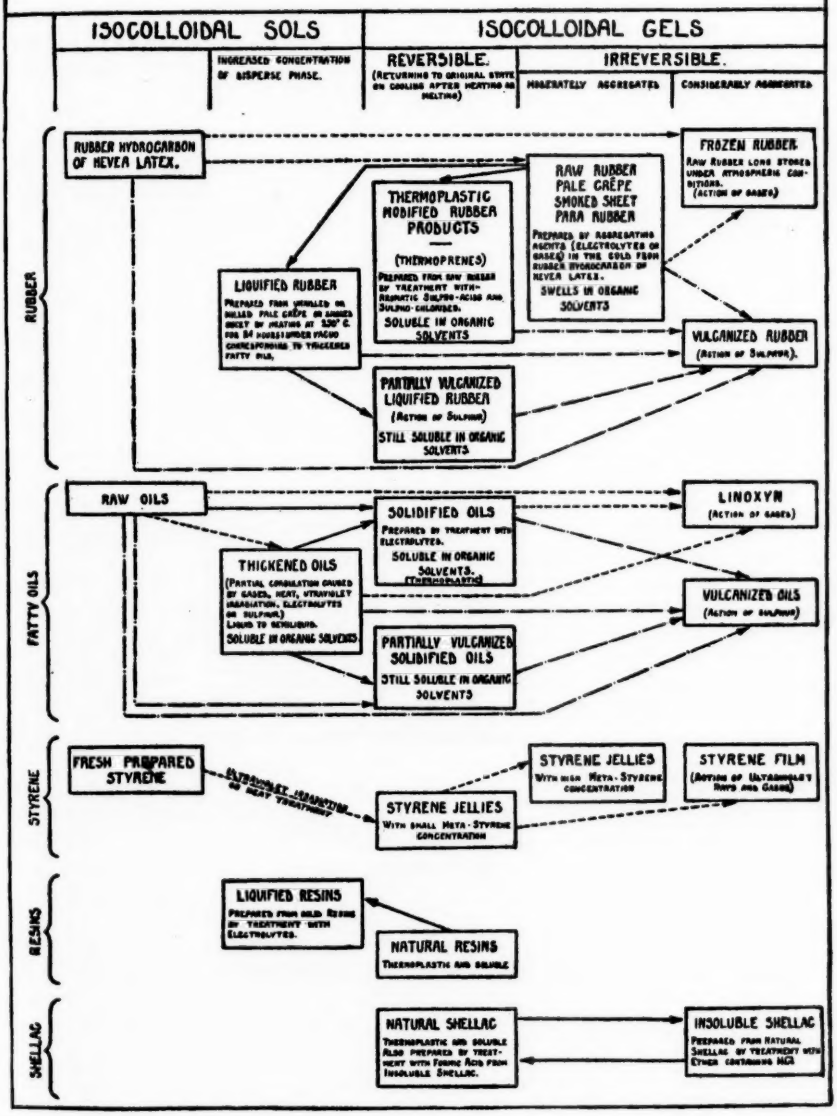
The Nos. 9212, 9117, 1925 and 2935, indicate various types of vulcanized solidified oil products.

The jelly system of a solidified fatty oil can be further aggregated. Sulfur aggregates solidified fatty oils in a similar way to that in which it aggregates rubber or raw fatty oils. As the solidifying process is to be considered as a partial aggregation it is obvious that the solidified oils would require much less sulfur for their vulcanization than the raw oil. When used as a raw material for varnishes the same should hold good in the behavior toward oxygen. This accounts for a varnish prepared from a solidified oil drying much quicker than a corresponding raw oil varnish, and for the same reason a solidified oil dried under the same atmospheric conditions adsorbs much less oxygen than the corresponding raw oil. The small adsorption power toward oxygen is the chief reason for the excellent aging properties of solidified oils. Such good aging properties can be observed in varnishes as well as in rubber mixes. If compounded in the proper way some of the vulcanized solidified oil products act as antioxidants on the rubber.

As the electrolyte treatment of fatty oils and of resins gave interesting results, it was decided to try the method with some other isocolloidal systems, especially with raw rubber itself, and it was found that the rubber jelly might also be influenced by the addition of electrolytes. The most important item was to discover the correct method of producing a dissolution of the electrolyte in the rubber. One of the most useful methods is to mill the electrolytes into the rubber and subsequently heat the mix. The products obtained are very similar to the gutta-percha-like, balata-like, and shellac-like thermoplastic rubber-conversion products of Fisher and the B. F. Goodrich Co. The electrolyte treatment of rubber was carried out by the author as a logical continuation of the above investigations and considerably before the first publication by Fisher and his collaborators appeared, and as the products he describes are similar to some obtained by the author, it

TABLE V

COLLOIDAL STATES OF ISOCOLLOIDS


ISOCOLLOIDAL SOLS
ISOCOLLOIDAL GELS
INCREASED CONCENTRATION OF DISPERSE PHASE.
REVERSIBLE. (RETURNING TO ORIGINAL STATE ON COOLING AFTER HEATING OR MELTING)
IRREVERSIBLE.
MODERATELY AGGREGATED
CONSIDERABLY AGGREGATED
RUBBER
RUBBER HYDROCARBON OF HEVEA LATEX.
FROZEN RUBBER
RAW RUBBER LONG STORED UNDER ATMOSPHERIC CONDITIONS. (ACTION OF GASES)
RAW RUBBER PALE CRÊPE SMOKED SHEET PARA RUBBER
PREPARED BY AGGREGATING AGENTS (ELECTROLYTES OR GASES) IN THE COLD FROM RUBBER HYDROCARBON OF HEVEA LATEX.
SWELLS IN ORGANIC SOLVENTS
THERMOPLASTIC MODIFIED RUBBER PRODUCTS
(THERMOPRENES)
PREPARED FROM RAW RUBBER BY TREATMENT WITH AROMATIC SULPHO-ACIDS AND SULPHO-CHLORIDES.
SOLUBLE IN ORGANIC SOLVENTS
LIQUIFIED RUBBER
PREPARED FROM UNROLLED OR MILLED PALE CRÊPE OR SMOKED SHEET BY HEATING AT 320° C. FOR 24 HOURS UNDER VACUO CORRESPONDING TO THICKENED FATTY OILS.
VULCANIZED RUBBER
(ACTION OF SULPHUR).
PARTIALLY VULCANIZED LIQUIFIED RUBBER
(ACTION OF SULPHUR)
STILL SOLUBLE IN ORGANIC SOLVENTS
FATTY OILS
RAW OILS
LINOXYN
(ACTION OF GASES)
SOLIDIFIED OILS
PREPARED BY TREATMENT WITH ELECTROLYTES.
SOLUBLE IN ORGANIC SOLVENTS. (THERMOPLASTIC)
THICKENED OILS
(PARTIAL COAGULATION CAUSED BY GASES, HEAT, ULTRAVIOLET IRRADIATION, ELECTROLYTES OR SULPHUR.)
LIQUID TO GEL-LIQUID.
SOLUBLE IN ORGANIC SOLVENTS
VULCANIZED OILS
(ACTION OF SULPHUR)
PARTIALLY VULCANIZED SOLIDIFIED OILS
STILL SOLUBLE IN ORGANIC SOLVENTS
STYRENE
FRESH PREPARED STYRENE
SPONTANEOUS POLYMERISATION OR HEAT TREATMENT
STYRENE JELLIES
WITH SMALL META-STYRENE CONCENTRATION
STYRENE JELLIES
WITH HIGH META-STYRENE CONCENTRATION
STYRENE FILM
(ACTION OF ULTRAVIOLET RAYS AND GASES)
RESINS
LIQUIFIED RESINS
PREPARED FROM GELD RESINS BY TREATMENT WITH ELECTROLYTES.
NATURAL RESINS
THERMOPLASTIC AND SOLUBLE
SHELLAC
NATURAL SHELLAC
THERMOPLASTIC AND SOLUBLE ALSO PREPARED BY TREATMENT WITH FUSING ACIDS FROM INSOLUBLE SHELLAC.
INSOLUBLE SHELLAC
PREPARED FROM NATURAL SHELLAC BY TREATMENT WITH ETHER CONTAINING HCl

Action of Gases. — Action of Sulphur. — Action of Modifying Agents.

may be of interest to discuss his publications from a colloid chemical standpoint (*Ind. & Eng. Chem.*, **19**, 1325 (1927)).

Fisher observed that when rubber was heated with sulfuric acid, chlorosulfonic acid, and organic derivatives of these acids, it changed into a tougher thermoplastic product which was, according to the reaction conditions, either gutta-percha-like, balata-like, or shellac-like. He considered his process to be an isomerization process of the rubber hydrocarbon and overlooked the fact that his products were poly-disperse systems in which the presence of the reagent or of the decomposition products of the reagent was as necessary as the presence of chromium and nickel in a chrome-nickel steel to give the modified properties. Fisher used, in most cases, a very large excess of reagent, so that, in addition to a certain adsorbed portion, an unnecessary excess of reagent remained. That this excess of reagent can be washed out without destroying the modifying action of the adsorbed portion does not prove that the reagent acts catalytically. The reaction is very similar to vulcanization in the absence of accelerators, in which case the sulfur not adsorbed (*i. e.*, free sulfur) can be removed by acetone extraction without disturbing the properties of the vulcanizate.

Fisher's reagents act on rubber similarly to electrolytes on fatty oils. In both cases during the process the amount of dispersed phase is increased. He proved the presence of a large amount of such disperse phase by dissolving the solidified rubber products in rubber solvents and precipitating with acetone a white powdery material. The percentage composition of the latter was identical with that of the pure rubber. The precipitated, powdery rubber hydrocarbon is very probably the real gel skeleton of the rubber jelly, just as metastyrene forms the gel skeleton of the isocolloidal system: styrene-metastyrene.

Both in the case of solidified oils and of rubber treated according to Fisher's method, the aggregative action of the reagent is a comparatively limited one, *i. e.*, the aggregation with the reagents used cannot go as far as with the aid of gases (for instance, oxygen), or with the aid of sulfur. The products are tougher than the starting material, but they do not lose their solubility in organic solvents. For this reason both the thermoplastic products of Fisher and the solidified oils may be further aggregated with the aid of sulfur, oxygen, and other gases, and the partial preaggregation accounts for the smaller concentration of sulfur or oxygen necessary to complete the aggregation.

The behavior of the thermoprene products toward organic solvents, *i. e.*, their improved solubility, is similar to the property of the oil, solidified by means of sodium sulfide, of being very easily emulsified in water. Such a property is very probably not caused by a lower degree of aggregation of the jelly, but by the higher affinity of the adsorbed reagent for the solvent than for the jelly in which it is adsorbed. It is, however, also theoretically possible that the solvents may be disaggregating agents in such cases, and further investigations in this direction are required.

In Table V is summarized the principal points mentioned in the text.

In conclusion, the author desires to express his thanks to Messrs. The British Dyestuffs Corporation, Ltd., in whose Rubber Service Laboratories the development of this work was carried out, and for permission to publish this paper.

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The Swelling of Rubber

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Some recent experiments on the diminution of the vapor pressure of solvents in rubber jellies, as well as measurements of swelling pressure, allow us to draw some conclusions as to the nature of the swelling phenomenon.

It has been found that, at the same concentration of rubber, the vapor pressure of rubber jellies from rubber of different origin was the same, and the previous mechanical working (mastication) of rubber had also no effect on this value (cf. Stamberger, *Rec. trav. chim.*, **47**, 316 (1928)). After the mechanical working, however, it swells in an unlimited manner, and gives as a resulting product up to a concentration of 30 per cent a more or less viscous liquid. This behavior shows that the solvent is not bound by surface adsorption and that there is a great resemblance to the process of molecular disperse solution. The three solvents used for these determinations were carbon disulfide, chloroform, and benzene. The same relative vapor pressure diminution was found when the concentration has been calculated as grams of rubber in 1 gram-molecule of solvent.

The shape of the curve in which the relative vapor pressure was plotted against the concentration differs from that expected according to Raoult's laws. The curves bend rapidly at a concentration of 20 to 30 per cent toward the vapor pressure axis. Although some resemblance to the ordinary process of solution was found, this behavior suggests a process of a more complicated nature. But the affinity of the solvent for the rubber can only be due to molecular forces.

Although no difference has been found between the vapor pressure of the "liquid" jelly of masticated rubber and the solid elastic jelly of untreated rubber, the swelling pressure of both showed big differences.

The liquid masticated rubber jelly had a swelling pressure of 35 cm. of mercury at a concentration of 0.4 gram of rubber in 1 cc. of solvent (toluene); the unmasticated rubber jelly had the same swelling pressure at a much lower concentration, 0.11 gram per cc.

This value shows that the swelling of a structureless (masticated) rubber differs greatly from the swelling of a rubber having a definite structure, although both show the same vapor pressure diminution. For this reason it is not possible to calculate the swelling pressure from the vapor pressure diminution on a simple thermodynamic basis.

This behavior shows that the forces which cause the imbibition of solvent by the jelly are not of a uniform nature, and the "structure factor" has an influence when the solvent is present in a liquid form (cf. Stamberger, *loc. cit.*).

Particulars of this investigation will be published shortly.

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Meaning and Measurement of Plasticity[1]

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ALTHOUGH the word "plasticity" is widely used in the arts and sciences, it has no definite quantitative meaning (*6*, *7*), yet the plastic properties of matter are of enormous importance in many industries. As scientific study of materials has increased, it has become more and more desirable to attain to a clearer idea of what is involved in this concept, to the end that plasticity may ultimately be quantitatively defined and measured.

The emergence of the word from common usage into the realm of technical words with well-defined meaning for quantitative considerations has been accompanied by considerable difficulty and confusion. Plasticity does closely relate to other properties of materials and the phenomena wherein plasticity may be an important factor are so varied that the role it plays may be overshadowed by and confused with the interplay of elastic and hardness phenomena on the one hand, and permanent set and viscous flow on the other. Reference to a few comments found in the literature will convince anyone of this. Van Rossem and Van der Meyden (*14*) have pointed out that plasticity involves more than deformation—that the amount of recovery is an essential element. Some seem to indicate that plasticity is synonymous with softness (*11*), or permanent set (*14*). Frequently the flow involved in the deformation is the all-engaging aspect and considerable confusion with viscosity has resulted (*1*, *2*, *16*). Inverse flow, or recovery, or "revertibility" is also to be considered. Loose and contradictory usage of the term exists in the rubber industry (*12*, *14*, *15*). A few attempt to use the term with the usual common-sensical meaning (*5*, *8*).

It does not help matters much to call plastic strain or plas-

[1] Presented before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

tic flow one of the three types of strains which are referred to as elastic, plastic, and pseudo-elastic (*3*). When the element of time is considered, all three of these classes merge into one another, since in the first there is quick and complete recovery, in the second no recovery, in the last slow recovery. The amount of deformation effected by a given force per unit area may have any value. The retention of the deformation may take place to any extent. Recovery may occur from perfectly complete to none; and from instantaneous to grossly and indefinitely slow. Whenever any property of matter, such as plasticity, that involves any of these factors is to be defined and measured, the quantitative definitions, the units, and the methods of measurement must allow for a gradation of the property from practically nil to an indefinitely great amount. Therefore, boundaries such as these for classification are difficult to set up and must remain diffuse. When a substance lies within the diffuse boundary region, as rubber does, it becomes of paramount importance to analyze clearly definitions and concepts. Within such regions and with such substances are to be found the severest tests for quantitative definitions and methods of measurement.

It is desirable to consider plasticity as an integral property of material and to base the quantitative definition and units and methods of measurement upon the integrated aspect of the phenomena involved in this property just as is done in practice in respect to viscosity and many other complex properties of materials. It is purposed to attempt this for plasticity if for no other reason than that it is extremely desirable to come to a clear and universal understanding regarding the definitions of certain mechanical properties of materials such as plasticity, softness, hardness, and permanent set, so that the concepts may become more serviceable and such properties be better controlled in the arts and industries.

Preliminary Definition

As an introductory and general definition more suited to the present purpose may be given this: *Plasticity is the susceptibility to and the retentivity of deformation.* The first aspect of plasticity refers to softness, the second to permanent set.

Plasticity by historical connotation refers somehow to the characteristics of matter that have to do with the receiving and the holding of form. In practice one must distinguish between two substances which, although equally soft and yielding with equal ease to the molding pressure, yet differ in the fidelity with which they hold shape when taken out of the mold. One may retain the mold contour accurately and permanently. The other may, within some interval of time, more or less prolonged, resume to a considerable extent its original or some other shape, determined by surface tension and other forces, quite unlike that which was im-

pressed upon it. The first is said to mold better—that is, to be more plastic than the second. The question is then—When any quantitative definition of plasticity is tentatively set up, how much should a substance be penalized in its degree of plasticity by virtue of the fact that, although it is not more stubborn in taking a new shape, it shows more variability and fickleness in holding it?

Degree of plasticity may be tested by means of sensations directly. One may judge the plasticity of a pellet of sculptor's clay or other plastic somewhat as follows: The pellet is held between the tips of the thumb and the forefinger and made to undergo some change of shape by pressure with the fingers. The force necessary to make any slight deformation is judged by the muscular effort in the fingers. The amount of deformation retained is judged by releasing the pressure at the finger-tips and observing whether or not the new shape is stable. If the deformation is given up, the actual sensation will tell that the displaced surfaces are following the retraction of the fingers. If a slight muscular effort was required to deform the pellet and if the deformation is retained by the pellet, then the pellet is said to be very plastic. The two aspects, ease of deformation and retention of form, are both felt. A substance is very plastic when it is easily deformed and when it retains the whole of the deformation given. No definition of and no mensural method for plasticity can be in contradiction with these facts.

Definition of Unit Plasticity

As a first suggestion of quantitative definition, the following is given: *A substance has unit plasticity that deforms a definite amount under some standard conditions when a force of 1 kg. per sq. cm. acts upon it for 1 second, and the whole of this deformation is permanently retained.* In this definition it is recognized that in measuring plasticity account must be taken of (1) magnitude of forces acting to give the deformation, (2) the amount of deformation retained, (3) the time during which the forces act (and time during which retention is desirable), (4) the conditions chosen as standard. The name "pla" is suggested for this unit.

Plasticity Measurement with New Plastometer

The definition of unit plasticity, with its various essential elements just enumerated, suggests more than one method of measurement. None of these need to be discussed for the present except that which concerns the new plastometer whose parts are described in detail in another paper (*9*), but whose operation, in a general way, will now be considered. For it the time factor is constant, the force is allowed to vary within certain limits, the deformation is variable within certain limits, and other conditions are kept constant.

The sample of the substances whose plasticity is to be measured is cut in the form of a small cylinder 1 cm. (0.394

inch) long and 1 cm. in diameter. This sample is placed between two jaws or fingers of the same diameters as the sample, the upper of which is movable vertically. A spring is then released which through a plunger causes the upper jaw to move downwards and impart to the sample a deformation (a change in height) depending upon its softness. The amount of this motion downwards is indicated on a dial, and is a measure of the force exerted by the spring in causing it. After this deformation has been produced, the force of the spring is suddenly removed. If the sample is very plastic according to the definition above, most of the deformation will be retained; if the sample has little plasticity and is quite elastic it will recover in short order and will retain little of this deformation. To measure the amount of this deformation that has been retained, a piston rests lightly upon the upper surface of the sample and remains in contact with it continuously, so that when the deforming force is suddenly released the amount of recovery is continuously indicated on a dial and may be read after 5 seconds.

This apparatus gives the magnitude of the force acting for a definite time, the amount of the deformation, and the portion of this deformation which is retained up to a definite time. It has thereby complied with all requirements of the quantitative definition for plasticity.

The force which the spring exerts during the deformation is related, inversely, to softness; i. e., the greater the force as indicated by the dial reading, the harder or stiffer the body. Let us call this force (in kg. per sq. cm.) F. The amount of the deformation retained, D (obtainable from dial readings), may be expressed in per cent of the initial length. Symbolically, then,

$$\text{the plasticity, } P, = C\frac{D}{F}$$

where C is a constant. In this first approximate quantitative expression there are only familiar things. F is some function of hardness determined under certain conditions, and D is some simple function of permanent set. Reflection upon the elementary sensations involved in everyday acquaintance with plasticity makes this seem rational. It is one of the simplest possible formulas suggestively defining plasticity. It may be looked upon as a general functional equation, however, and the next step is to establish just what the functions are.

Plasticity is defined, then, as the product of two functions D and s, where s is a function of softness and D a function of permanent set. The simplest case is to let the function s be equal to the softness itself, and to let D be the permanent set. Although there is good justification for the first, certain other possibilities present themselves in place of the second.

$$P = sD$$

The amount of deformation retained may be expressed in per cent of the total amount of deformation given irrespective of the magnitude of the forces involved and of the dimensions of the specimen. The word "retentivity" is suggestive here and will be tentatively adopted. The material which retains the whole of any deformation is rated 1; one that retains none is rated 0. In the first case the plasticity is entirely determined by the softness; in the second the plasticity remains zero irrespective of the softness. An illustration of the first class is the sculptor's clay; of the second, a steel spring. For the present one may rest content to suggest how some formulation may be reached for softness and retentivity in their simplest setting.

Letting h, h_1, h_2 be, respectively, the initial height, the height under compression, and the recovered height, the change in height during compression expressed in terms of the initial height is $\frac{h-h_1}{h}$. The more or less permanent change in height of the body at some definite time after the force has been removed is $\frac{h-h_2}{h}$. The ratio of these is

$$\text{Retentivity} = \frac{h-h_2}{h} \Big/ \frac{h-h_1}{h} = \frac{h-h_2}{h-h_1}$$

To arrive at some rational expression for softness is more difficult but more urgent, not only for the present inquiry into the nature of plasticity, but more fundamentally as a step toward an examination and understanding of the concept hardness. A sensual impression of softness seems to be associated directly with the yielding of material when touched or pressed. It has no regard for certain other properties; for instance, one may with propriety speak of a soft steel spring that is very elastic as well as of a soft clay that is very inelastic. There are no specific dimensional elements implied. We may compare the softness of a feather bed with that of a mat or of wax even without taking into account any dimensions, and we may compare the softness of two spring mattresses without taking into account the length of the springs. Softness sensually is an integral and gross property of a material. A "specific softness" is desired for the formulation of plasticity. Hardness, the reciprocal of softness, in the rubber industry is measured by effects of compressional forces. It is often called resistance to penetration, since the force is applied over a very small area of the sample.

As a first suggestive formulation the following may be used:

$$\text{Softness, } s, = K \frac{h-h_1}{h} \times \frac{1}{F}$$

where K is a constant of the apparatus and units employed. This implies that the greater the force F required for a given deformation, the harder the body; or for any given force

or range of forces, the smaller the deformation, the harder the body. The range of hardness allowed is from zero to indefinitely great. When comparing samples over extended ranges of force or for some force F far removed from the conditions implied in the definition, allowance must be made for an exponent of F. This holds true also for the factor of time and perhaps for all other factors that are changed when conditions are changed. Plasticity becomes as a first approximation:

$$P = K \frac{h - h_1}{hF} \times \frac{h - h_2}{h - h_1} = K \frac{h - h_2}{Fh}$$

The above analysis is the result of an attempt to give a logical background to the proposed scheme of measurement. This certainly is preferable to a perfectly arbitrary method of procedure (*10*).

The Time Factor

The time of compression in the definition is one second. In the practical apparatus the compression goes from a minimum to a maximum in that interval. An average value is used in calculating the absolute plasticity. In the original development of the apparatus it was deemed for such small intervals of time advantageous to use a spring rather than weight, especially if one is interested in sudden release of the compressing force. The release need not be so sudden as in this apparatus. The particular intervals used should be set by the article under observation. From a broad technical view it would be desirable, however, to have all measurements of plasticity refer to some standard condition so that the values for any material that may be recorded may be comparable. Other considerations entered into the adoption of a rather short interval. One is from the viewpoint of flow. It is desirable to have any corrections which may be necessary due to small changes in the dimensions of the sample approximately proportional to the force. If the times involved are so short that equilibrium conditions of viscous flow cannot be established, or can play only a minute part, then one may expect to have simple relations. Certainly, when conditions of equilibrium for viscous flow have been established, changes in the initial dimensions of the sample may not bear any simple linear relation to the changes in the forces applied to bring about a given flow or deformation. By these statements it is not meant that plasticity may not and should not be obtained at longer lapses of time, but only that, if so made, there may be difficulty in referring back to the values obtained for the shorter intervals designated in the definitions. Either arbitrary extrapolation

Note—This is difficult so long as the various factors involved are not known, and accurate interpolation is impossible. There is demanded a knowledge of how deformation varies with the dimensions of the body, with the force applied, and with the time and temperature; and furthermore, how the recovery from deformation depends upon these parameters.

may be made or a great deal more of the properties of materials must be learned.

No doubt one may at times wish to determine plasticity under extreme conditions. When plasticity is measured for purposes of control in the factory, the conditions under which measurements are made and the magnitude of factors must be so chosen that the results may readily be shown to have some simple interpretation in practice. In case of the milling and mixing of rubber and its compounds, the time intervals involved are generally very small—less than one second. For this reason also the time intervals were kept as small as practicable in the first instrument. A final point in favor of the short interval was the fact that it appears that short intervals are involved in the estimation of the property "nerve" to which experienced rubber craftsmen are wont to refer. In "nerve" not only the completeness of recovery and the magnitude of the forces exerted during recovery, but also the speed of recovery appears to enter.

Range of Usefulness of Plasticity Measurements

It may be of some interest to point out that one may be concerned with plasticity under conditions that may not pertain only to compression. Bending or torsional or extensional forces and deformations may be involved, and also changes of volume. The concepts and analysis given above may be directly applied to such cases.

Plasticities of Some Common Materials

(Temperature, except in case of rubber, 20° C.)

Material	Softness[a]	Retentivity	Plasticity *Milliplas*
Chewing-gum:			
Unmasticated	0.342	0.722	243
Masticated 15 times	0.284	0.843	2410
Masticated 30 times	0.256	0.814	2070
Beeswax, commercial	0.0545	0.25	13.6
Asphalt	0.0211	0.20	4.22
Cheese, Swiss	1.57	0.0424	66.4
Bread, rye	11.41	0.547	6250
Bread, rye, crust	4.40	0.0206	90.8
Beef, raw, stewing	2.54	0.211	537
Veal, raw, chop	2.27	0.289	757
Bologna, ring	4.28	0.313	1342
Steel, cast (*12*)	0.0000121	0.0278	0.00034
	0.0000129	0.0992	0.0013
Crude rubber; smoked sheet, unmasticated:			
30° C.	1.16	0.0748	8.73
100° C.	1.66	0.0305	50.7
140° C.	2.02	0.0692	139.9

[a] The unit of softness assumed in this table is that of a body of standard dimensions (1 × 1 cm.) when 1 kg. per sq. cm. compressing it for 1 second will produce a 10 per cent change in height. Some relative unit is always implied in such a table as this, even if it is not explicitly mentioned.

The measurement of plasticity is of interest wherever the forming of articles in molds is concerned, and whenever it is desired to use deformable materials under conditions where there is not time for the equilibrium conditions of viscous flow to be set up; and even in certain cases where the interest lies rather in elasticity, such as in upholstery or felts. In cases like the latter, plasticity is an objectionable feature and its measurement may indicate how nearly this unde-

sirable feature may have been eliminated. Industries which deal in plastic materials, as the ceramics industries; which have to do with the manufacturing of bakelite and casein articles and the like; also those dealing in the cellulose, have interest in plastometric measurements for control purposes. The measurements of plasticity may possibly be of some importance to the paper industry and certain textile industries. Plasticity should play some role in the pastry and confectionery industries. Incidentally, plasticity is a very important property of all materials that are to be masticated between teeth—that is, most foods. This suggests that the rate of change of plasticity in chewing-gums on being masticated between the teeth may be of some importance to the chewing-gum industry.

The critical study which led to the analysis of plasticity given in these pages was begun in connection, not with rubber, but with certain metallurgical problems involved in the working of metals, such as the drawing of tungsten and molybdenum. These concepts should have a direct bearing upon ductility and malleability and other working qualities of metals, for these properties also have to do with the molding of materials to predetermined shapes under certain practical situations in respect to the applications of the forces and the time intervals involved. Certainly, here again the factors of deformability and retentivity are concerned. In the case of wire drawing, the deformability factor may be thought of in several ways—one as follows: During the process of drawing through a die there is an orientation and alignment of the crystals. One set of the 110 planes, for example, in cubical systems such as tungsten become more nearly parallel to each other and to the direction of drawing. This alignment may be followed by use of x-ray technic and the degree of orientation estimated. The amount of orientation per unit of tractive force per unit of cross-sectional reduction is a measure of this deformability. The retentivity factor may be considered as the ratio of the difference between the initial and the final diameters of the wire and the difference between the initial diameter of the wire and the diameter of the die. The time element should be considered—either maintained constant at some arbitrary value, or the function of time determined and proper allowance made when going from one set of conditions to another involving a change of time intervals.

The temperature coefficient of plasticity of some materials such as rubber, of other thermoplastics and even of metals, and possibly of cheoplasts, has practical importance. In the rubber industry plasticity is a property of enormous importance. A large amount of data has been gathered with the use of the instrument described above bearing upon the relation of plasticity to the time and to other elements entering into the mastication of rubber, and upon the temperature coefficient of plasticity. Such data are given by Dieterich

elsewhere in this issue (*4*). The thermal coefficient of plasticity may vary enormously depending both upon the pigments used and the treatment to which the rubber has been subjected during the milling and mixing operations. The plasticity rating of some common materials is indicated in a preliminary fashion in the accompanying table. The plasticity of steel is estimated from data given by Unwin (*13*). The compression in one case was 0.0157 per cent, in the other 0.118 per cent. The time factor is ignored. It is not known how to extrapolate the scale of softness for large ranges of time nor how the retentivity depends upon time factor in the deformation and in the recovery processes. Linear variation of deformation with force is implied. All these assumptions tend to make the figures higher than should be.

Literature Cited

(1) American Society for Testing Materials, Standards and Tentative Standards, Rept. of Committee E-8 on Nomenclature and Definitions, 1928; also Rept. of Technical Committee III on Plasticity, Consistency, etc., 1928.
(2) Bingham, "Fluidity and Plasticity," p. 4 (1922).
(3) Bingham, *J. Franklin Inst.*, **197**, 99 (1924).
(4) Dieterich, IND. ENG. CHEM., **21**, 768 (1929).
(5) Dubrisay, *Rev. gén. mat. plastiques*, **3**, 289 (1927).
(6) Hatchek, *Chemistry Industry*, **47**, 835 (1928).
(7) Jeffries, "Science of Metals," p. 155.
(8) Jeffries, *op. cit.*, pp. 13 and 148.
(9) Karrer, IND. ENG. CHEM., Anal. Ed., **1**, 158 (1929).
(10) Malam, *Instrument World*, **1**, 155 (1928).
(11) Maxwell, "Theory of Heat," p. 295 (1883).
(12) Park, Carson, and Sebrell, IND. ENG. CHEM., **20**, 278 (1928).
(13) Unwin, "Testing of Materials of Construction," p. 274 (1910).
(14) Van Rossem and Van der Meyden, Rept. of International Congress for Testing Materials, 1927.
(15) Williams, IND. ENG. CHEM., **16**, 364 (1924), describes the plastometer mentioned by these authors.
(16) Winkelmann and Croakman, *Rubber Age*, **22**, 474 (1928).

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A New Plastometer[1]

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AT THE Swampscott meeting of the AMERICAN CHEMICAL SOCIETY an analysis was given of the meaning of plasticity when this term names a property of solids that concerns the molding of plastics such as rubber.[2] A function for plasticity was deduced with some suggestions on the adoption of a C. G. S. unit of plasticity. Also, a design of a plastometer, based upon this analysis, was outlined. It is the purpose of this paper to give a full description of such a plastometer.

Original Plastometer

A detailed drawing of the instrument as first conceived in February, 1927, is given in Figure 1. The rubber sample, 1, in the form of a cylinder 1 cm. long, 1 sq. cm. cross section, is held between two vertical round rods, A and B, which will be designated as upper and lower plungers. These plungers consist of contacting end caps, 15, 20, of steel mounted upon porcelain tubes, 19, which in turn are cemented into sockets 16, 21. The lower socket, 21, slides through a bushing 22. Its nether end is cut obliquely, and by means of a spring is pressed into contact with the surface of a cylindrical wedge, 23, movable in and out by means of a drum nut, 25, fitted to the threaded end, 24, of the wedge. The height of the sample may be read to 0.001 inch off the scale on the drum nut, 25. The upper socket, 16, slides in a tube, 17, and has a bearing shoulder for the spring, 9, called the force spring. The upper plunger, together with other parts bearing upon it from above, is carried by a light spring, 27.

Toggle joint 8 is actuated by a power spring, 10, that is restrained in a tube and exerts directly against the head 13, of a double compression rod, 12. This power spring is com-

[1] Received June 18, 1929.

[2] This analysis and some preliminary data obtained with this instrument will appear in the August issue.

pressed or charged by the levers, 11, and may be released by a slight motion of a latch 2. When such release of the power spring takes place, the piston, 13, pushes the toggle from the flexed to, and through, the vertical position and depresses the piston, 18, a constant amount, and compresses the force spring, 9, to an extent depending upon the hardness of the sample. The amount of compression of the force spring and sample is indicated by the gage hand, 6, which carries a friction hand, 14, to its maximum position. The position of the friction hand may be read later to obtain

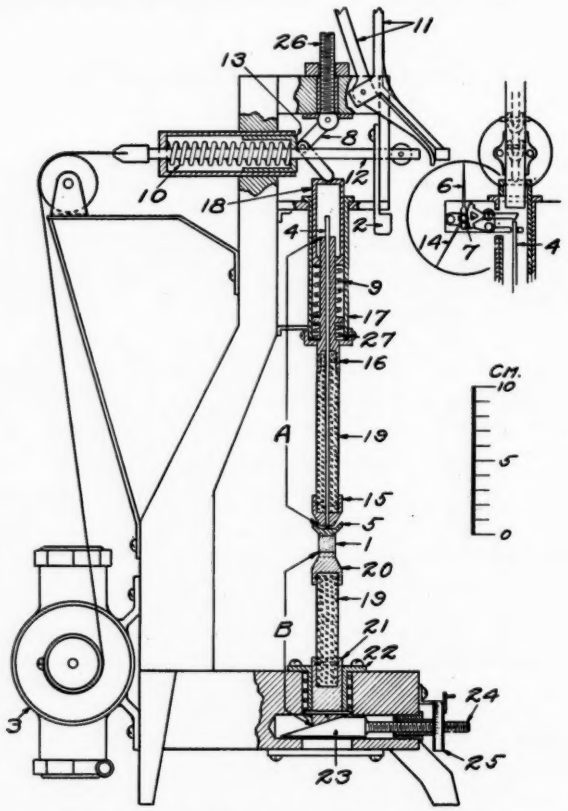

Figure 1—Sectional View of Original Plastometer

the extent to which the sample has been compressed and with what force this has been brought about. The gage has connection with the sample by means of an extension rod, 4, of glass or invar. The gage in the present apparatus was especially constructed to fit the situation. Its essential parts were the gears, 7, of a small pressure gage. To control the time of one stroke—that is, of the time during which the compression is applied—the power spring, 10, was caused to expand against the dampening resistance offered by an

ordinary Yale door check, 3. This interval turned out to be about 0.6 rather than 1 second as intended.

The procedure is as follows: A sample with a plate, 5, laid upon it, is inserted between the plungers. The wedge scale reading indicating the height is recorded; the latch lever, 2, is pushed to release the power spring, 10, which had been compressed before the sample was inserted. The resulting downward motion of the upper plunger depends upon the softness of the sample, and is readable from the

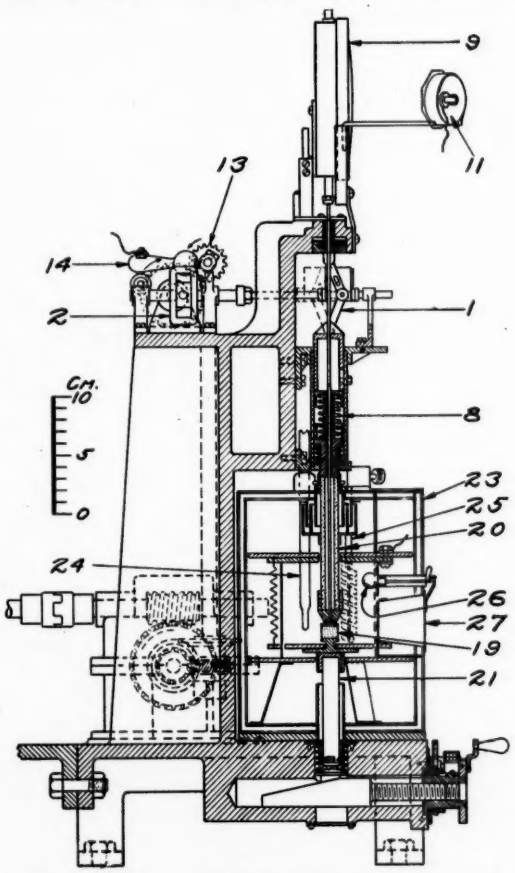

Figure 2—Sectional View of Automatic Plastometer

position of the friction hand, 14. The stop watch is started the moment the motion of the friction hand ceases. The traveling hand, 6, is observed in its motion backwards and its position read after 5 seconds. From the three scale readings thus recorded the plasticity may be reckoned. The dial reading of the maximum hand gives directly the amount of compression, $h - h_1$, where h is the original height, h_1 the height under maximum compression. Next, the force, F,

that has been exerted to accomplish the compression is also obtained by subtracting the dial reading given by the friction hand from the dial reading which indicates a perfectly soft body—that is, the reading which indicates that the compression spring has experienced no resistance from the sample and was free to follow to the extreme downward position demanded by the toggle. The amount of the compression, which is retained at the end of 5 seconds, is $h - h_2$, where h_2 is the height 5 seconds after compression.

In accordance with the definition that has been given in

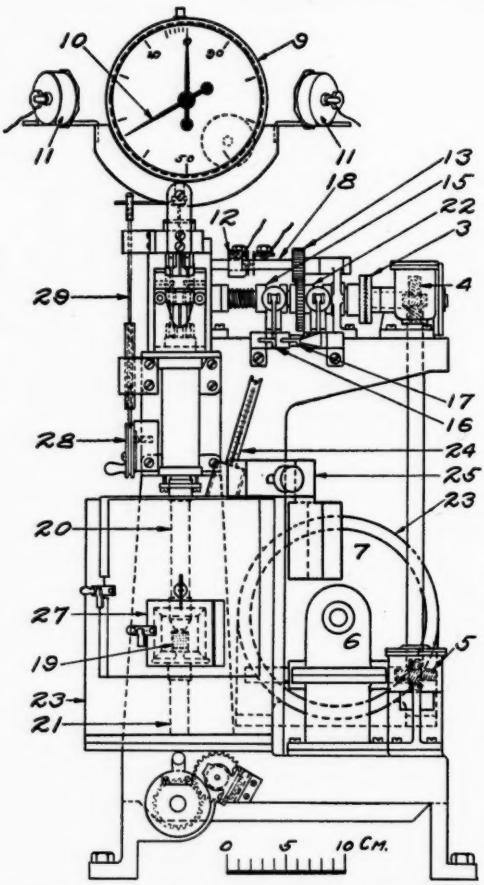

Figure 3—Front View of Automatic Plastometer

the analysis, plasticity is the product of a softness function and a property termed retentivity. It may be expressed as follows:

$$P = K \times \text{softness} \times \text{retentivity}$$

$$= K \times \frac{h - h_1}{hF} \times \frac{h - h_2}{h - h_1} = K \frac{h - h_2}{hF}$$

where K is a constant depending upon the units and apparatus. In calculating the absolute values from the readings of this instrument, the average value of force, F, is used.

Automatic Plastometer

The plastometer that has just been described has been modified in certain respects to eliminate the personal element to a great extent and to make the control of the time interval more positive. It was originally intended to make this instrument entirely automatic and autographic. The autographic feature has been eliminated from considerations of practicality. A gage has been substituted, whose reading, however, has been made much simpler as will be seen below. Figures 2, 3, and 4 depict in sectional, front, and top views

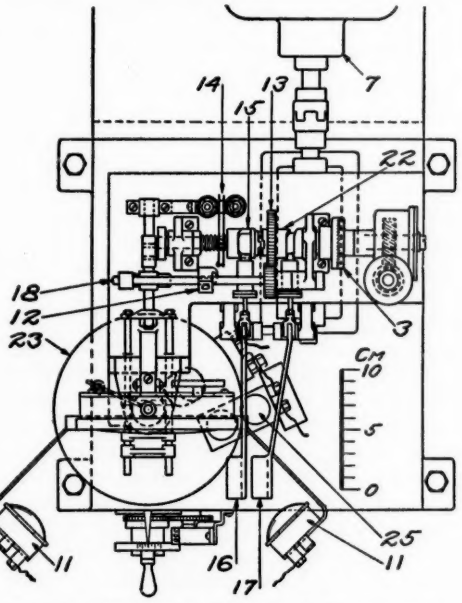

Figure 4—Top View of Automatic Plastometer

the instrument with these changes. The toggle joint, 1, is operated through the scotch yoke and eccentric, 2, by means of a sawtoothed clutch, 3, and a system of gears, 4, 5, 6, and a synchronous motor, 7. The gearing is such that the toggle, 1, will go through one-half cycle of operation—that is, from the extreme left to the extreme right positions in 1 second. It is positively driven in both its to-and-fro motions so that it does not, as in the previous instrument. release the force spring, 8, suddenly. The gage, 9, is, as in the previous instrument, furnished with a friction hand, 10, which retains the maximum position to which the indicating hand moves. The indicating hand may be read at any time after the maximum compression has been accomplished.

To facilitate this, a light signal is provided by means of lamps, 11. This signal, flashing every second, is distinctly visible while the indicating hand is being followed in its motion backwards. The making and breaking of the signal circuit are accomplished by the use of Ford induction coil contacts, 14, and a hard-rubber cam, 12, whose shaft is geared, 13, to that of the scotch yoke. The engaging and disengaging at the clutch, 3, depends upon the lever, 17, which when depressed raises a pin out of its groove in a sleeve, 22, and allows the driven half of the clutch to slide into engagement with the driving half. As long as there is engagement the timing shaft will be rotated by means of the gears, 13. The yoke shaft may or may not be rotated depending upon whether or not the sleeve, 15, is allowed to slide into engagement with the end of the clutch sleeve just mentioned. When the lever 16 is depressed, such sliding of this sleeve will take place. When the levers, 16 and 17, are depressed momentarily, the scotch yoke shaft will make one-half revolution, while the signal shaft, 18, will make one complete revolution. By prolonged depression of the levers, 16 and 17, any number of revolutions may be allowed—that is, any number of the to-and-fro motions of the toggle, any number of compressions, and any number of light signals may take place. By momentary depression of the yoke-sleeve lever, 16, and prolonged depression of the clutch-sleeve lever, 17, only one motion of the toggle is allowed, but any number of revolutions of the signal shaft may take place. This means that a sample may be compressed for 1 second and its recovery observed after one or any whole number of seconds. The gage, 9, is of a special design. Its stem, as well as other parts, is hollow. It has only a small hair-spring to take up lost motion. This makes for extreme lightness and a small load upon the sample. The dial of this gage is graduated to 0.001 inch; the extreme travel of the stem is 0.5 inch. To lift gage extension rod, 4, off the sample, the eccentric wheel, 28, bearing against a lifting rod, 29, is provided.

To control the temperature of the sample, 19, the upper and lower plunger, 20, 21, are surrounded by an oven, 23, equipped with thermometer, 24, and thermostat, 25. The samples are inserted and removed through a small door. Illumination within the furnace is provided for by a small lamp, 26, above the small door, 27, and attached to the large door.

Only stocks that do not recover completely in 1 second may be studied with this instrument.

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Time and Temperature-Plasticity Relations for Crude Rubber as Measured with the Goodrich Plastometer[1]

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KARRER (*2*) has presented the fundamental principles guiding the quantitative measurement of plasticity of materials, and has described a plastometer (*1*) whose design and operation incorporate these basic principles. The simple relationship between softness, permanent set, and plasticity, when the time interval of compression is kept short, was pointed out. This relationship makes it an easy matter to interpret the results obtained by the use of this instrument and to make intelligent comparisons of different materials, or of the effects of different kinds of treatment of the same material.

The results recorded below, all of which refer to crude rubber, and which are typical of rather extensive data, illustrate the applicability of the plastometer to the requirements of the rubber industry, and their bearing on progress in rubber technology is indicated. The plasticities have not been expressed in absolute units, since relative values, based on the changes of dimensions of the sample during compression and recovery, are entirely adequate for factory control work. Multiplying these values by the factor 0.01876 gives the absolute plasticity in kilogram-centimeter-second units.

Change of Plasticity of Crude Rubber with Time of Milling

MASTICATION OF DIFFERENT KINDS OF RUBBER—The data in Table I, which are plotted in Figure 1*a*, were obtained

[1] Presented before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

during the course of some mastication tests and refer to 200-pound (91-kg.) batches milled on a 24 by 84 inch (61 by 213 cm.) smooth roll mill. The mill roll setting was kept constant at $^{9}/_{32}$ inch (7 mm.) and the cooling water regulated to give the same rate of temperature rise in each batch so that milling conditions might be as nearly as possible alike for all batches. Comparisons were made of pale crepe, smoked sheets, and latex-sprayed rubbers.

Unless stated otherwise, all measurements were made at 100° C. and, whatever the temperature, the samples were preheated for 20 minutes before they were put into the plastometer.

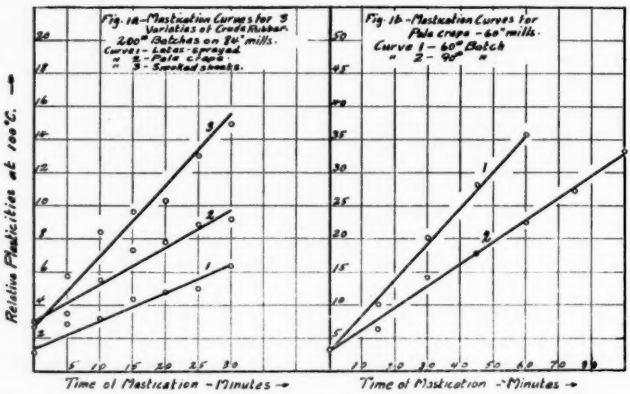
Fig. 1a—Mastication Curves for 3 Varieties of Crude Rubber. 200# Batches on 84" mills. Curves 1 - Latex-sprayed. " 2 - Pale crepe. " 3 - Smoked sheets.
Relative Plasticities at 100°C.
Time of Mastication - Minutes
Fig. 1b - Mastication Curves for Pale crepe - 60" mills. Curve 1 - 60# Batch " 2 - 90# "
Time of Mastication - Minutes

Table I—Relative Plasticities at 100° C. of Different Kinds of Rubber for Various Periods of Mastication

Time of Mastication	Pale Crepe	Smoked Sheets No. 1	Latex-Sprayed No. 1
Minutes			
0	2.9	2.7	1.1
5	3.4	5.7	2.8
10	5.5	8.3	3.1
15	7.3	9.6	4.3
20	7.7	10.2	4.7
25	8.8	13.0	4.9
30	9.1	14.9	6.3
Final batch temperature	227° F. (109° C.)	227° F. (109° C.)	233° F. (112° C.)

It is evident that the rates of breakdown of these three varieties of rubber differ enormously. There is considerable scattering of the experimental values, but this is to be expected when small samples are taken from large batches—i. e., the deviations are due to variations in different parts of the batch. The personal factor introduced by cutting the bank through the mill also influences the regularity of the results. For small batches, as illustrated in Figure 1*b*, the scattering is much reduced. A straight line fits the points as well as any other smooth curve, which means that the rate of mastication of rubber, for relatively short intervals at least, is uniform and directly proportional to the time of milling. This linear relation, unquestionably, does not hold for very long

masticating periods, and is related to the batch size and the method of manipulation on the rolls.

EFFECT OF BATCH SIZE—Some typical results are shown in Table II and Figure 1*b*. These data relate to 20 by 60 inch (51 by 152 cm.) smooth roll mills operated at 1/8-inch (3-mm.) opening. A 60-pound (27-kg.) batch on these rolls gives a fairly small bank, the greater part of which is rolling. A 90-pound (41-kg.) batch, on the other hand, produces a bank which is largely stationary. Theoretically, the extent of mastication is directly proportional to the number of times the rubber passes between the rolls, so a 90-pound batch should require 50 per cent more cutting back and forth and a 50 per cent longer time on the rolls to reach a plasticity equivalent to that attained by a 60-pound batch at any given time. This is verified to a satisfactory degree by the experimental data, the final plasticity of the 90-pound batch being practically equal, in 90 minutes, to that of a 60-pound batch at the end of 60 minutes, the former having been cut through the mill 50 per cent oftener.

Table II—Relative Plasticities of Pale Crepe at 100° C. in Different Batch Sizes for Various Periods of Mastication

TIME OF MASTICATION	60-LB. (27-KG.) BATCH	90-LB. (41-KG.) BATCH
Minutes		
0	3.3	3.3
15	10.1	6.2
30	20.3	14.1
45	28.2	17.8
60	35.7	22.4
75		27.1
90		33.5

A satisfactory linear relationship between plasticity and period of mastication is again observed in this case, although the latter is 1 1/2 hours. In fact, we have noted this proportionality for milling times as long as 2 hours. Such a simple relationship between milling time and plasticity does not hold for any other type of plastometer, and the ease of calculating milling time in terms of equivalent plasticities is clearly evident.

Temperature Coefficient of Plasticity

References in the literature to the effect of temperature upon the properties of rubber leave the impression that in the neighborhood of 70° C. the plasticity undergoes a sudden change and that above this temperature rubber is, in fact, a different material in this respect than it is at lower temperatures. Thus, Van Rossem and Van der Meyden (*3*) speak of rubber as being "fully plastic" at 70° C., but only "partially plastic" below this temperature. Table III and Figure 2 illustrate the manner in which temperature affects the plasticity of masticated smoked sheets, and these data are typical of many measurements. In no case has a discontinuity, or abrupt change, been found in plastic properties at or near 70° C.; the variation with temperature is of degree rather than of kind.

Table III—Relative Plasticities of Masticated Smoked Sheets at Various Temperatures

Temperature ° C.	No Softener Added	Softener Added
30	6.4	14.0
50	14.1	24.3
75	24.9	49.0
100	56.2	101.0

As shown by the curves, the temperature coefficient of plasticity gradually increases as the temperature is raised. In the first case the temperature coefficients are found to be 0.35, 0.75, and 1.50 per degree Centigrade for the temperature intervals of 30–40°, 70–80°, and 90–100° C., respectively. In the other instance, in which a softener was added, the corresponding values are 0.42, 1.50, and 2.45. This change in the temperature coefficient of plasticity is a confirmation of the desirability of low-temperature mastication, for at temperatures below, say, 60° C., the internal stresses set up in the rubber are high and rapid breakdown occurs, while at higher

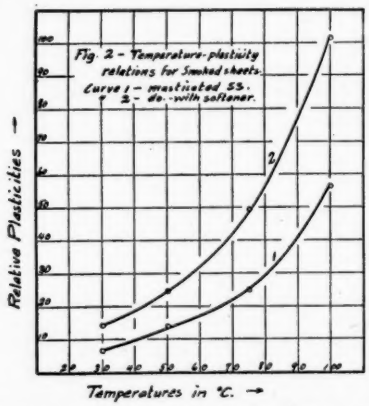
Fig. 2 - Temperature-plasticity relations for Smoked sheets.
Curve 1 - masticated 55.
" 2 - do. - with softener.
Relative Plasticities
Temperatures in °C. →
2
1

temperatures the internal resistance to deformation rapidly decreases, and little permanent softening of the rubber results.

The instrument has proved a powerful tool in the study of mastication, mixing, calendering, and tubing problems, some of the results of which, it is hoped, will be published in the near future. In speed and simplicity of operation it leaves little to be desired. The fact that the true plasticities, as measured with the instrument, are directly proportional to the figures which express them—a plasticity of 20, for example, indicates a material which is exactly twice as plastic as one for which the figure is 10—makes it possible to set up a convenient scale which is easily understood by machine operators with no technical training. This is of immense importance in factory control and can be accomplished at the present time by no other plastometer.

Literature Cited

(1) Karrer, Ind. Eng. Chem., Anal. Ed., **1**, 158 (1929).
(2) Karrer, Ind. Eng. Chem., **21**, 770 (1929).
(3) Van Rossem and Van der Meyden, Rept. of International Congress for Testing Materials, 1927.

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Effect of Stearic Acid on Various Crude Rubbers

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DURING the last few years considerable work has been done in determining the effect of increasing amounts of stearic acid in various types of compounds using different accelerators. The work described herein emphasizes the point that in comparisons of this kind a third variable may enter—namely, the crude rubber—and if fine distinctions are to be drawn as to the correct amount of stearic acid to use with any particular accelerator some consideration should be given to possible variations in the rubbers used.

Russell (*1*) shows that when different crude rubbers are cured with zinc oxide certain samples give compounds with very poor physical properties while other samples give good results. He connects the tendency to give well-cured compounds with the ability of the rubber to dissolve zinc oxide. He further showed that those rubbers that do not give good properties can be brought up to normal by adding small amounts of various fatty acids, and thus, in a qualitative way at least, indicated the importance of organic acids to the vulcanization process.

About the same time Whitby (*2*) showed that the resins that occur naturally in rubber consist largely of fatty acids, such as stearic, oleic, and linoleic. His figures indicate that the amount of such acids varies appreciably even within any one grade and type of rubber and that there is no direct relationship between the resin content and the acid content. If all the acid is figured as stearic acid, he shows for first-grade plantation rubbers acid contents of from 0.50 to 1.92 per cent on the rubber; for lower grades it usually runs lower. He gives a mean value of 1.35 per cent acid for plantation grades and further states that types of rubber other than Hevea usually contain little or no free acid.

In later work Whitby and his co-workers (*3*, *4*) study the effect of adding increasing amounts of organic acid to rubber that has been extracted with acetone until it is practically resin-acid free and then compounded with several type accelerators. They show a varying effect with different accelerators and also indicate that the effect may be appreciable when organic acids are added even within the normal acid range for Hevea rubber samples. A summary of the previous work that has been done by other investigators on the influence of fatty acids on vulcanization is also given by Whitby and Evans (*3*).

Experimental Procedure

Various grades of rubber were selected in order to obtain a range of acid values. Each grade was blended on a mill to obtain uniformity and then an average sample taken for the acid determination. For this purpose 30 grams were extracted with acetone and the extract was then titrated with alcoholic potash. Instead of using Whitby's designation "acid number" (milligrams of KOH to neutralize the acid from 100 grams of rubber), all results have been figured as though the resin acids were entirely stearic acid and the acid content is then given as per cent stearic acid on the rubber.

Results

Some of the results obtained by using these rubbers of known acid value in several type formulas are given below. The results have been compressed to show tendencies in as few comparisons as possible rather than to give actual detailed results, as the purpose of this paper is to indicate a condition and no attempt has been made to cover the whole ground of possible variations.

RUBBER-SULFUR—Table I shows four rubbers of varying acid content used in the simple formula 100 rubber and 10 sulfur. Each stock was cured with and without 1 per cent of added stearic acid. The tensiles and moduli are shown for three cures of each set. It is noted that in this type formula the addition of 1 per cent stearic acid had very little effect on either tensiles or moduli, although, if anything, there is a slight tendency to lower both.

RUBBER-SULFUR-ZINC OXIDE-DIPHENYLGUANIDINE—Table II gives three rubbers in a diphenylguanidine formula both with and without the addition of 1 per cent stearic acid. In this case the high resin-acid rubber (smoked sheet) shows a very noticeable drop in physical properties when 1 per cent stearic acid is added, while the other two rubbers are practically unaffected. The total acid in the case of the smoked sheet becomes appreciable after the 1 per cent stearic is added (2.36 per cent on the rubber).

RUBBER-SULFUR-ZINC OXIDE-HEPTENE—Table III covers

Table I—100 Rubber, 10 Sulfu

Cure at 50 lbs. (3.2 kg. per sq. cm.) steam pressure (148° C.)	90 Minutes		105 Minutes		120 Minutes	
Tensile in lbs. per sq. in. (kg. per sq. cm.)	Break	800% Elong.	Break	800% Elong.	Break	800% Elong.
	SMOKED SHEET—1.36% RESIN ACID					
Control	2050 (144.1)	1100 (77.3)	2350 (165.2)	1400 (98.4)	2450 (172.3)	1650 (116.0)
+ 1% Stearic acid	1950 (137.1)	1000 (70.3)	2250 (158.2)	1325 (93.2)	2400 (168.7)	1600 (112.5)
	AMBERS—0.79% RESIN ACID					
Control	2200 (154.7)	1300 (91.9)	2400 (168.7)	1800 (126.5)	2600 (182.8)	2100 (147.6)
+ 1% Stearic acid	2150 (151.2)	1250 (87.9)	2350 (165.2)	1700 (119.5)	2600 (182.8)	2050 (144.1)
	ROLL BROWN—0.20% RESIN ACID					
Control	1350 (94.9)	750 (52.7)	1650 (116.0)	1000 (70.3)	1800 (126.5)	1250 (87.9)
+ 1% Stearic acid	1300 (91.9)	700 (49.2)	1575 (110.7)	900 (63.3)	1750 (123.0)	1200 (84.4)
	CAUCHO BALL—0.12% RESIN ACID					
Control	1050 (73.8)	500 (35.1)	1150 (80.8)	750 (52.7)	1350 (94.9)	900 (63.3)
+ 1% Stearic acid	1000 (70.3)	500 (35.1)	1200 (84.4)	650 (45.7)	1350 (94.9)	850 (59.7)

Table II—100 Rubber, 6 Zinc Oxide, 3.5 Sulfur, 1 Diphenylguanidine

Cure at 35 lbs. (25 kg. per sq. cm.) steam pressure (138.5° C.)	30 Minutes		40 Minutes		50 Minutes	
Tensile in lbs. per sq. in. (kg. per sq. cm.)	Break	600% Elong.	Break	600% Elong.	Break	600% Elong.
	SMOKED SHEET—1.36% RESIN ACID					
Control	2800 (196.8)	1600 (112.5)	3050 (214.4)	2150 (151.2)	3350 (235.5)	2600 (182.8)
+ 1% Stearic acid	2500 (175.8)	1300 (91.9)	2800 (196.8)	1550 (108.9)	3100 (217.9)	1800 (126.5)
	EARTH SCRAP—0.20% RESIN ACID					
Control	2650 (186.3)	1100 (77.3)	2900 (203.9)	1350 (94.9)	3000 (210.9)	1500 (105.5)
+ 1% Stearic acid	2600 (182.8)	950 (66.8)	2850 (200.4)	1200 (84.4)	2950 (207.4)	1435 (103.7)
	ROLL BROWN—0.20% RESIN ACID					
Control	2050 (144.1)	850 (59.7)	2350 (165.2)	1100 (77.3)	2450 (172.2)	1200 (84.4)
+ 1% Stearic acid	2000 (140.6)	800 (56.2)	2400 (168.7)	1050 (73.8)	2500 (175.8)	1200 (84.4)

the same comparison as the previous one except that an aldehyde-amine type of accelerator (heptene) is used in place of diphenylguanidine. Here again the high resin-acid smoked sheet shows a decrease in physical properties on the addition of stearic acid. But when the low resin-acid rubbers are considered, it is seen that the addition of stearic acid improves both the tensiles and moduli very appreciably and if anything the rubber with the lowest natural acid content shows the greatest improvement. The total acid in these three low acid rubbers is 1.12 to 1.2 per cent on the rubber.

Table III—100 Rubber, 6 Zinc Oxide, 3.5 Sulfur, 0.5 Heptene

Cure at 35 lbs. (2.5 kg. per sq. cm.) steam pressure (138° C.)	30 Minutes		40 Minutes		50 Minutes	
Tensile in lbs. per sq. in. (kg. per sq. cm.)	Break	600% Elong.	Break	600% Elong.	Break	600% Elong.
Smoked Sheet—1.36% Resin Acid						
Control	2700 (189.8)	1250 (87.9)	3100 (217.9)	1700 (119.5)	3150 (221.5)	1900 (133.6)
+ 1% Stearic acid	1800 (126.5)	750 (52.7)	2400 (168.7)	1050 (73.8)	2700 (189.8)	1500 (105.5)
Earth Scrap—0.20% Resin Acid						
Control	1000 (70.3)	150 (10.5)	850 (59.7)	200 (14.0)	1000 (70.3)	250 (17.5)
+ 1% Stearic acid	1600 (112.5)	400 (28.1)	1850 (130.0)	500 (35.1)	2100 (147.6)	1050 (73.8)
Roll Brown—0.20% Resin Acid						
Control	750 (52.7)	250 (17.5)	1050 (73.8)	350 (24.6)	1200 (84.4)	400 (28.1)
+ 1% Stearic acid	1850 (130.1)	575 (40.4)	2150 (151.2)	800 (56.2)	2400 (168.7)	900 (63.3)
Caucho Ball—0.12% Resin Acid						
Control	800 (56.2)	250 (17.5)	1050 (73.8)	350 (24.6)	1200 (84.4)	400 (28.1)
+ 1% Stearic acid	1650 (116.0)	600 (42.2)	2150 (151.2)	800 (56.2)	2400 (168.7)	900 (63.3)

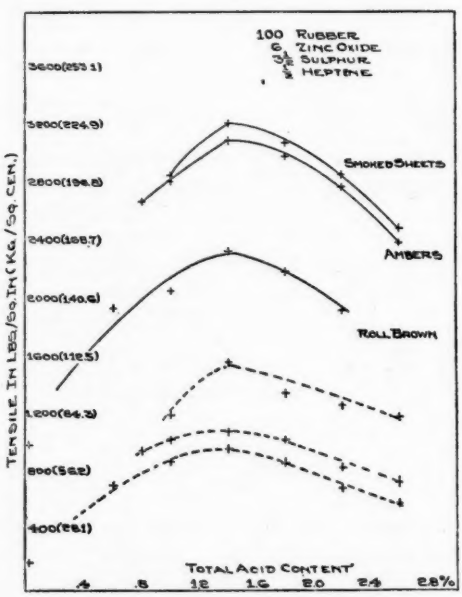

Figure 1

Combination of High Acid and Low Acid Rubbers—Table IV gives the heptene formula using (1) a high acid smoked sheet, (2) a mixture of 2 parts of high acid smoked sheet and 1 part low acid roll brown, (3) a mixture of the same two rubbers, but in the ratio 1 of smoked sheet to 2

of roll brown, and (4) the low acid roll brown alone. The total resin-acid values of the mixtures are also shown for each rubber combination. Here again there is a lowering of tensile and modulus when stearic acid is added to the high acid smoked sheet and a raising of these properties when this acid is added to the low acid roll brown. The two compounds containing the mixed rubbers show an increase of the physical properties roughly in proportion to the amount of low acid rubber present—i. e., to the lack of natural resin acids.

HEPTENE FORMULA WITH INCREASING AMOUNTS OF TOTAL ACID—In Figure 1 the heptene formula is shown using three different rubbers and increasing amounts of stearic acid so that the total stearic acid (resin acid plus added acid) varies from 0.2 to 2.6 per cent on the rubber. Stearic acid was added on the mill to give definite increases in total acid. Tensile and modulus at 600 per cent elongation curves are shown for a 40-minute cure at 35 pounds (2.5 kg. per sq. cm.) steam with three rubbers of varying amounts of resin

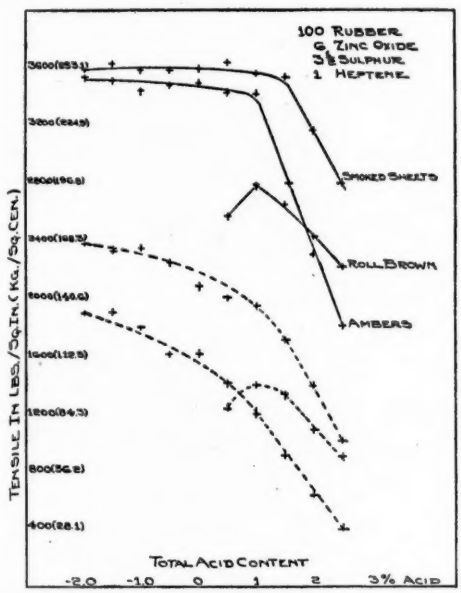

Figure 2

acid. The amount of resin acid present in each rubber is indicated by the first point at the left in the curve for the rubber. It is noted that in this formula all three rubbers show a quite definite maximum for both physical properties at a total acid content of approximately 1.4 per cent on the rubber, and that there is a falling off in tensile and modulus as the acid content varies on either side of this figure.

Table IV—100 Rubber, 6 Zinc Oxide, 3.5 Sulfur, 0.5 Heptene

Cure 40 minutes at 35 lbs. (2.5 kg. per sq. cm.) steam (138.5° C.)

Resin acid, per cent	Smoked Sheet 1.36		2 Smoked Sheet 1 Roll Brown 0.97		1 Smoked Sheet 2 Roll Brown 0.88		Roll Brown 0.20	
Tensile in lbs. per sq. in. (kg. per sq. cm.)	Break	600% Elong.	Break	600% Elong.	Break	600% Elong.	Break	600% Elong.
Control	3100 (217.9)	1700 (119.5)	1800 (126.5)	550 (38.7)	1400 (98.4)	400 (28.1)	400 (28 1)	200 (14.1)
+ 1% Stearic acid	2400 (168.7)	1050 (73.8)	2400 (168.7)	700 (49.2)	2200 (154.7)	650 (45.7)	1600 (112.5)	700 (49.2)

HEPTENE FORMULA VARYING TOTAL ACID FROM PLUS TO MINUS—A heptene formula is shown in Figure 2 using three different rubbers and varying the amount of total acid (resin and added) between the limits −2.0 to +2.5 per cent on the rubber by adding on the mill the desired quantity of either stearic acid or alcoholic potash. The points shown are for equivalent states of cure; i. e., as alkali is added it is necessary to take a shorter time of cure to compensate for the accelerating effect of the alkali. In this case 1 per cent heptene is used in place of the 0.5 per cent used previously and this apparently tends to throw the acid maximum a little lower—nearer to 1 per cent acid. At approximately 1 per cent total acid there is a rather definite point of inflection on all the curves. Continued decrease of acid below this point does not cause a lowering of physical properties as was obtained in the previous figure, probably because the added alkali forms soap with the acid which tends to hold up the physical properties.

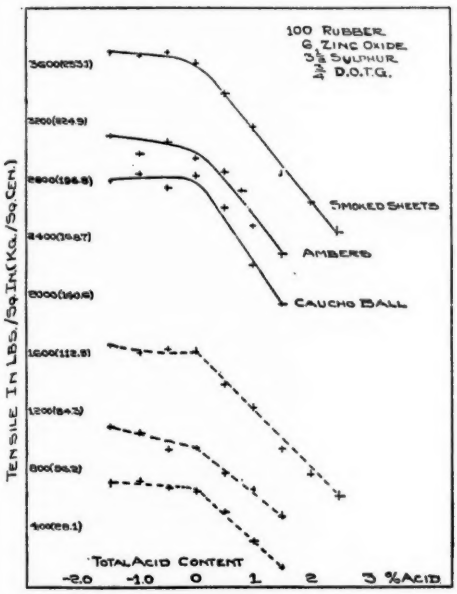

Figure 3

DI-*o*-TOLYLGUANIDINE FORMULA AS ABOVE—This comparison as given in Figure 3 covers the same ground as the one just shown except that di-*o*-tolylguanidine is used as the accelerator in place of heptene. In this case the point of flexing in all three curves appears to be close to zero acid content. There is very little change in physical properties as the acid content is increased above this.

Conclusions

The exact acid content of a compound has an important effect on the physical properties secured with it and there is probably a definite state of acidity for each accelerator, and perhaps compound, which gives the best results with the combinations in question.

The naturally occurring resin acids in rubber must be considered in figuring the total available acid in any compound. This is especially important where changes are made from one type or grade of rubber to another.

Acknowledgment

Acknowledgment is due to G. W. Cassell, formerly of The Fisk Rubber Company Research Laboratory, who conducted most of the experimental work covered in this paper.

Literature Cited

(1) Russell, U. S. Patent 1,467,197 (September 4, 1923).
(2) Whitby, *India Rubber J.*, **68**, 617 (1924).
(3) Whitby and Evans, *J. Soc. Chem. Ind.*, **47**, 122T (1928).
(4) Whitby and Greenberg, IND. ENG. CHEM., **18**, 1168 (1926).

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Stearic and Oleic Acids as Rubber-Compounding Ingredients

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IT IS proposed in this brief discussion to touch upon the relative effects of stearic and oleic acids in a few typical rubber stocks; then to discuss certain anomalies as to the effect of stearic acid on chemical and physical cure; and, lastly, to consider some of the differences found by use of different accelerators.

Inasmuch as oleic acid is the chief impurity in commercial stearic—running from 10 to 15 per cent—it seems desirable to know the behavior of oleic acid alone.

Comparison of Stearic and Oleic Acids

The following data show the comparative effects of double-pressed stearic and commercial oleic acids in typical rubber compounds:[1]

Table I—Action of Stearic and Oleic Acids in Typical Rubber Compounds

Captax Tread—4 parts acid on 100 rubber
23 volumes black
1 volume ZnO
Best cure, 70 minutes at 127° C. (260° F.)

	Stearic	Oleic
Cure at 127° C., minutes	70–100	70–100
Modulus at 300 per cent, kg. per sq. cm.	68–90	61–75
Acid bloom after 15 hours[a]	None	Very bad

Captax Friction—0.6 part acid on 100 rubber
1/2 volume ZnO
8 parts softener
Best cure, 40 minutes at 127° C.

	Stearic	Oleic
Cure at 127° C., minutes	40–50	40–50
Modulus at 700 per cent, kg. per sq. cm.	85–97	78–85
Acid bloom[a]	None	No bloom, but very sticky

Zinc Oxide Friction—2 parts acid on 100 rubber
7 1/2 volumes ZnO
4 1/2 parts softener
Best cure, 30 minutes at 127° C.

	Stearic	Oleic
Cure at 127° C., minutes	30–40	30–40
Modulus at 300 per cent, kg. per sq. cm.	63–78	53–68
Acid bloom[a]	None	No bloom, but more tacky than control

[a] Uncured stock.

[1] This work was done by R. W. Beveridge of the compounding staff of the Goodyear Tire & Rubber Co.

From these data it would appear that, in Captax stocks, there is a distinct loss in modulus due to the substitution of stearic acid by oleic. This seems to be more pronounced in the loaded stocks. From the point of view of acid bloom, the tread stock was the only one giving trouble, but this is serious. It would thus appear that purified stearic acid might be desirable for carbon black stocks, whereas for friction stocks, where modulus is not always so important, less pure stearic could be used, particularly if additional tack is desired. It must be borne in mind that these conclusions are, so far, limited to Captax.

Behavior of Stearic Acid

Let us now turn to stearic acid itself. We will note a few things about its behavior with zinc oxide and carbon black. It is necessary to distinguish between the effect on physical and chemical cure. This is shown by some unpublished work by C. R. Park, a summary of which is given in Tables II and III.

Bracketed ingredients denote original materials in the rubber mix (except rubber). Material appended to bracket by plus sign is that which gives the effect on cure noted in the adjoining columns. Physical cure picked by hand. Vol. = volume loading on 100 volumes rubber; blk = micronex carbon black; acid = stearic acid; stiff. = modulus as shown by stress-strain curve.

Table II—Effect of Stearic Acid on Physical and Chemical Cure

Composition	Combined Sulfur	Physical Cure	Stiff
[25 vol. blk. + 8 pts. S] + 4 acid	Same	Same	Less
[25 vol. blk. + 8 pts. S] + 3¾ vol. ZnO	Inc. 70%	Inc. 15%	Inc. 70%
[25 vol. blk. + 8 pts. S + 3¾ vol. ZnO] + 4 acid	Inc. 15%	Inc. 15%	Inc. 3%
[20 vol. blk. + 3 pts. S + 1 vol. ZnO + 1.2 Captax] + 4 acid	Dec. 8%	Inc. 50%	Inc. 40%
[6 pts. S] + 1 vol. ZnO	Same	Inc. 16%	Inc. 40%
[3 pts. S + 1 vol. ZnO + 1.2 Captax] + 4 acid	Curves cross	Dec. 20%[a]	Curves cross
[10 pts. S] + 1 vol. ZnO		10% faster	Inc. 50%
[10 pts. S] + 4 acid		20% slower	50% less
[10 pts. S + 1 vol. ZnO] + 4 acid		Same	30% Inc.
[3½ pts. S + 1 vol. ZnO] + 4 acid		Slight Inc.	Slight Dec.
[3½ pts. S + 1 vol. ZnO + 4 acid] + 0.5 Captax		Cures 1/10 time	Great Inc.
[6 S] + 1 vol. ZnO		Inc. 10%	Inc. 100%
[6 S + 1 vol. ZnO] + 4 acid		Dec. 10%	Inc. 20%
[6 S + 1 vol. ZnO + 4 acid] + 0.25 Captax		Inc. 90%	Inc. 600%

[a] See Figure 1.

Table III—Comparison of Stiffening Effect of Zinc Oxide and Black

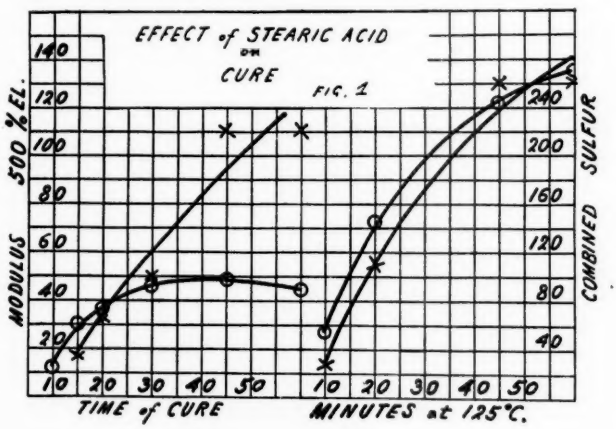
	(Kg./cm.²) @ 700%
6 S + 1 vol. ZnO	52
6 S + 1 vol. Micronex	25
6 S + 1 vol. Thermatomic	26

Here we see that if stearic acid is added to a sulfur mix there is a marked decrease in chemical and physical cure. In a sulfur-black stock the cure is unchanged but the stiffness is

decreased. Moreover, while the addition of one volume of zinc oxide to a sulfur or sulfur-black stock speeds up the cure and markedly increases the stiffness (double what one volume of black alone will do), the further addition of stearic speeds up chemical cure but has little further effect unless the sulfur is high (10 per cent).

The addition of stearic to a sulfur-zinc-Captax stock shows a large increase in the physical cure and stiffness for the black stocks and a softer stock at low cures for the non-black changing to stiffer as cure increases. The chemical cure is retarded in both cases.

Hence it would seem that stearic acid is, by itself, a retarder of chemical and physical cure. With zinc oxide it changes to an accelerator of chemical cure and with Captax to an accelerator of physical cure. Here, however, even in the presence of zinc, the chemical cure is retarded.



Action of Other Accelerators

The writer has previously published (*1*) a so-called accelerator classification which considered various typical groups of accelerators. The following remarks will apply to these groups only:

Work with extracted rubber shows: (1) All accelerators are improved by zinc oxide; (2) the zinc oxide must be rendered rubber-soluble by stearic acid except in the case of the dithiocarbamates and the thiurams which are capable of reacting directly with zinc oxide; (3) Captax and derivatives must have zinc in soluble form to function at all; (4) P-nitroso will function in extracted rubber in the absence of zinc oxide but, if zinc oxide is present, it must have stearic also. Hence it would seem that the prime function of stearic acid is to furnish zinc oxide in a suitable form for the use of the accelerator. Otherwise it acts as a softener and retarder. As to why an excess of stearic acid retards diphenylguanidine and has no such action on other accelerators, it is hard to

say. Perhaps there is a more or less stable diphenylguanidine stearate formed which is a non-accelerator. Certainly there is much to be explained as to the mechanism of the zinc soap in the physical cure of rubber.

Literature Cited

(1) Dinsmore and Vogt, *Trans. Inst. Rubber Ind.*, **4**, 85 (June, 1928); *Rubber Age*, **23**, 554 (1928).

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Effect of Increased Quantities of Stearic Acid on Tread Abrasions

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THE problem of laboratory abrasion tests on rubber which will allow one to predict something regarding the relative service of two tread compounds on the road is a very important one and has been attacked by many investigators.

Perhaps the best machine so far developed is the Grasselli abrader, invented by Williams (*3*) who states that "the Grasselli abrader is a machine for measuring the volume loss of rubber per unit of work expended. Its principle is similar to that of a Prony brake in which the rubber test pieces are similar to the friction surfaces of the brake." The abrasion index secured by the Williams method represents volume abraded, in cubic centimeters per horsepower-hour. The volume abraded is the volume loss of both test pieces and the horsepower-hour figures refer to full brake horsepower.

While the Grasselli abrader is perhaps the best abrasion machine now in existence, its results should not be taken as a final criterion. Williams states: "While the Grasselli abrader makes possible a real comparison of the abrasion resistance of any compound, it should not be expected to replace actual road tests." This sensible admonition has been disregarded by too many rubber technologists. The results obtained on this machine have been interpreted in ways not intended and conclusions have been drawn which are not correct.

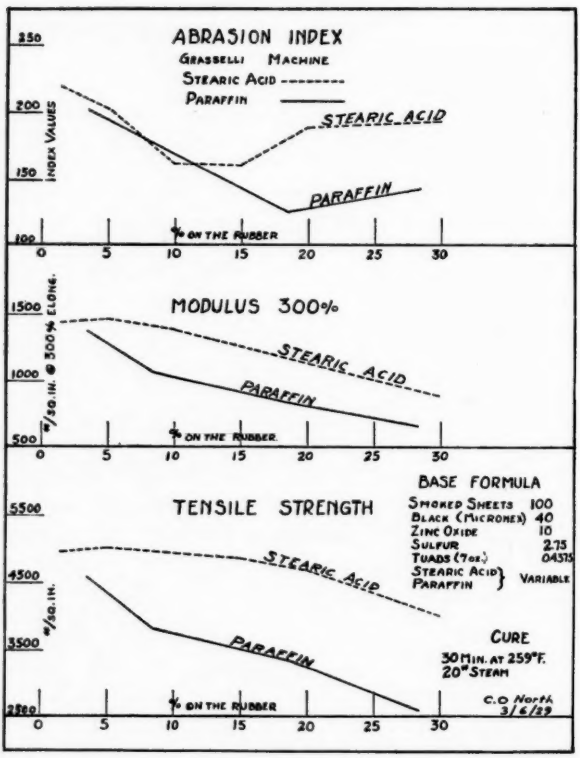
It is well known that the introduction of certain higher fatty acids—e. g., stearic—into rubber compounds is beneficial. A deficiency is thus supplied and a uniformly vulcanizing compound is secured. Furthermore, stearic acid aids in the dispersion of pigments, such as carbon black. There is no question but that the moderate use of stearic acid in tread compounds is decidedly helpful.

However, there are people who believe that if a little is

good, more is better. Stearic acid has been added as high as 9 per cent on the rubber. The resulting compounds gave, on the Grasselli abrader, index values much below what one would normally expect. It should be explained that the lower the index value—i. e., the less the volume loss per unit of power consumed—the better the tread, since the tire whose tread wears the longest is usually considered the most desirable.

Experimental

Any test which is applied beyond its reasonable limitations is dangerous. One simple method of attack is the "reduction to absurdity" procedure; this was followed.



A tread compound which vulcanizes nicely at low temperatures was selected (formula given on accompanying graph). Stearic acid was added in quantities from 1.5 to 30 per cent on the rubber. Batches were milled in the regular way and sheets and abrasion blocks vulcanized for 30 minutes at 126° C. (259° F.)(20 pounds steam). This cure was selected as previous work had shown it to be the optimum. Abrasion tests were made in accordance with the procedure recom-

mended by Williams. Stress-strain curves were secured in the usual manner. The accompanying graph shows the variation in tensile strength, modulus (load necessary to produce 300 per cent elongation), and abrasive index with increased quantities of stearic acid.

It will be noted that the abrasive index falls until a minimum is reached at 10 per cent. This value is held until 15 per cent, when it begins to increase. It should also be noted that the value for 30 per cent stearic acid is less than that for 2 per cent, which is the normal quantity usually employed. In other words, if we are to believe the results, we should expect better tread wear, other things being equal, from the stock containing 30 per cent stearic acid than for the one containing 2 per cent.

The above did not appear to be a reasonable conclusion. The stocks from 3 per cent up, on examination were found to be rather heavily covered with stearic acid "bloom;" i. e., the stearic acid came to the surface and thus provided a lubricant, which interfered with the proper working of the test.

One's first thought on the subject would naturally be that lubrication of the surface should not materially affect the test because the index of abrasion represents volume abraded per horsepower-hour. But Plummer and Beaver (*1*) and also Vogt (*2*) have shown that only a small percentage of the power input goes to do true abrasion work. Therefore, lubrication of the surface should be expected to have an effect. In this case the waxlike properties of stearic acid probably are responsible for the low values obtained.

To check this still further, a number of experiments were made with paraffin. This substance is an old well-understood compounding ingredient. It blooms heavily and has never been suspected of promoting abrasive resistance. In fact, it is known to have a contrary effect.

Paraffin was added in varying amounts from 3.5 to 28.5 per cent on the rubber. At 18.5 per cent paraffin an abrasion index of 125 was secured. This is lower than any value obtained in the stearic acid series. Furthermore, the modulus and tensile strength values are both decidedly affected. Therefore, it would appear that the results are highly absurd and the test is in error chiefly because of the surface lubrication afforded by the wax which blooms to the surface.

Conclusion

The only conclusion justified, therefore, is that, in so far as abrasion index is concerned, we must fall back on road tests. There the values depend, not only upon the abrasion resistance of the tread, but also upon the design of the tire, its load, position on the car, etc. The Grasselli abrader is of value in laboratory work, but the results must always be carefully scrutinized and must be interpreted within the actual conditions of test.

Acknowledgment

The data contained in this paper were secured in the Akron laboratory of this company by Arnold H. Smith and C. O. Wheeler.

Literature Cited

(1) Plummer and Beaver, IND. ENG. CHEM., **20**, 895 (1928).
(2) Vogt, *Ibid.*, **20**, 140, 302 (1928).
(3) Williams, *Ibid.*, **19**, 674 (1927).

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Effect of Stearic Acid on Reclaimed Rubber

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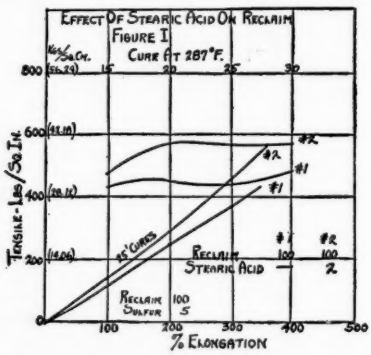
IT IS the purpose of this paper to discuss the effect of stearic acid on the process of manufacture of reclaimed rubber and its effect when used with reclaimed rubber in vulcanized rubber goods. The uses of stearic acid in reclaimed rubber can best be grouped as follows: (1) in the digester or heater as a plasticizing agent to speed up the disaggregation of the rubber; (2) when added to the plasticized rubber on the mill or in an internal mixer, to facilitate addition of a pigment or to impart some desirable property or consistency; (3) in compounds containing substantial amounts of reclaimed rubber.

In most reclaiming processes softeners are used in the devulcanizer in conjunction with heat, to aid in plasticizing the rubber. They may also be added on a warm-up mill or in an internal mixer to give a reclaim with desirable properties for tubing machine and calender operations. It may be desirable to have a definite amount or a complete absence of tack. It is therefore essential that the right softener is used and that it is added at the proper time. Factory conditions such as type of equipment, method, and speed of processing and cooling conditions determine the limits of firmness, softness, tackiness, plasticity, milling properties, and nerve of the reclaimed rubber required by the rubber goods manufacturer.

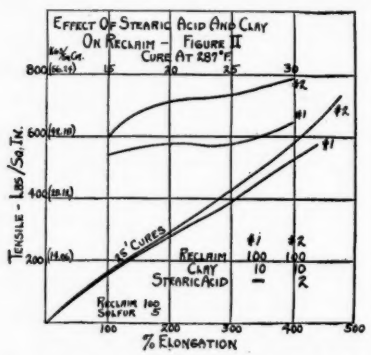
Effect of Softeners in Alkali Whole-Tire Reclaim

DIGESTER PROCESS—Table I shows some of the chemical and physical tests ordinarily run on samples of reclaim. Three experimental reclaims were prepared from the same lot of whole-tire scrap by the alkali process. In one case no oil was used for softening purposes, in the second 4 per cent of pine tar was added, and in the third 4 per cent stearic acid. The same amount of 6 per cent sodium hydroxide solution was used in each experiment. The samples were

devulcanized 14 hours at 160 pounds (4.2 kg. per sq. cm.) steam pressure. As indicated by the comparative chloroform extracts and plasticity coefficients, the first reclaim was dry and harsh. It was very slow to break down on the mill and difficult to keep around the roll until broken down. The second reclaim using pine tar was much softer. Its consistency was about the same as that of an average high-



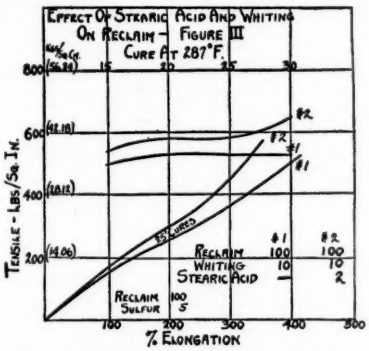
grade whole-tire reclaim. The curing properties are improved. The third reclaim using stearic acid was also dry and harsh. On the mill it broke down slightly better than the reclaim containing no softener. The stearic acid is practically all converted to sodium stearate in the alkali process. This has no softening action and under these



conditions has a drying action and removes all trace of "tack." This effect is obtained quite generally with the fatty acid soaps. In the alkali process of reclaiming, stearic acid does not have an opportunity of functioning as a softener because it is immediately converted to a soap. In the preparation of heater or digester reclaims in which no caustic soda is used, stearic acid functions as a softener.

Heater Process—Table II shows physical test data on three reclaims prepared by the heater process. The fiber-free

ground treads were heated for 16 hours at 130 pounds (9.1 kg. per sq. cm.) steam pressure without softener and with 5 per cent of pine tar and 5 per cent of stearic acid. The stock softened with pine tar approached proper consistency while the reclaim made without softener and the reclaim made



with stearic acid were quite harsh. The reclaim using stearic acid was more plastic in its milling properties than the reclaim using no softener. It was smoother and more compact with less tack than the sample using pine tar although not so plastic.

Table I—Effect of Softeners in Alkali Whole-Tire Reclaim—Digester Process

	No Oil		4% Pine Tar		4% Stearic Acid	
	(1)	(2)	(1)	(2)	(1)	(2)
	%	%	%	%	%	%
Acetone	8.25	8.38	8.63	9.64	7.23	7.41
Ash	18.14	18.26	17.76	17.90	16.83	16.80
Chloroform	25.40	24.90	29.82	28.07	25.98	25.15
Plasticity, *K*	5.73		4.68		6.01	

Reclaim 100, sulfur 5%

Cure at 141.6° C.	Tensile strength		Elong.	Set	Tensile strength		Elong.	Set	Tensile strength		Elong.	Set
Min.	*Kg./cm.²*	*Lbs./in.²*	%	%	*Kg./cm.²*	*Lbs./in.²*	%	%	*Kg./cm.²*	*Lbs./in.²*	%	%
15	50.1	713	420	23	59.4	844	435	22	44.5	634	387	15
20	43.8	623	390	15	55.0	780	410	16	39.6	564	325	11
25	37.7	536	367	12	43.8	623	340	13	37.8	538	350	12
30	37.1	528	360	12	46.0	654	340	12	35.4	503	317	11
35	40.5	576	370	10	48.2	685	370	15	36.8	524	320	10

STRESS-STRAIN

Elong. %	*Kg./cm.²*	*Lbs./in.²*	*Kg./cm.²*	*Lbs./in.²*	*Kg./cm.²*	*Lbs./in.²*
100	12.0	171	10.4	148	10.4	148
200	16.8	239	20.4	291	17.4	248
300	27.0	384	36.6	520	31.4	446

Effect of Stearic Acid Added to Plasticized Rubber

The second use for stearic acid is for incorporation into the reclaimed rubber after devulcanization. After treatment in the digester, the plasticized rubber is washed, dried, and sent to the mill room for the refining, straining, and leaf sheeting operations. The softener may be added at any convenient time after washing. Prior to refining a softener may be added in an internal mixer to effect further plasticization or to facilitate dispersion of a pigment which is to be refined

into the reclaim. The reclaim now has a low alkali content and the stearic acid in this case acts as such and imparts to the reclaim some very desirable properties. Approximately four volumes of various pigments were refined into a whole-tire reclaim with and without addition of stearic acid to determine the effect of stearic acid on physical properties, plasticity, etc.

Table II—Effect of Softeners in a Heater Process Tire Reclaim

	No Softener	5% Pine Tar	5% Stearic Acid
	Devulcanized 16 hours at 130 lbs. (9.1 kg. per sq. cm.)		
	%	%	%
Acetone	12.20	12.86	12.76
Ash	16.04	14.93	15.24
Chloroform	18.39	22.07	24.60
Specific gravity	1.132	1.125	1.127
	Reclaim 100, sulfur, 5%		

Cure at 141.6° C.	Tensile strength		Elong.	Set	Tensile strength		Elong.	Set	Tensile strength		Elong.	Set
	Kg./	Lbs./			Kg./	Lbs./			Kg./	Lbs./		
Min.	cm.²	in.²	%	%	cm.²	in.²	%	%	cm.²	in.²	%	%
15	25.7	366	290	8	25.7	366	357	8	28.8	410	297	10
20	26.0	369	250	4	24.0	341	303	4	28.9	411	255	6
25	28.6	407	243	4	30.5	434	310	7	32.8	466	247	9
30	29.9	425	215	2	29.2	415	260	4	31.5	448	227	6
40	29.4	418	187	4	32.9	468	220	4	33.2	472	200	5
50	31.4	446	205	4	33.1	471	230	4	35.2	500	180	3
K			5.62				4.94				5.59	
Recovery, per cent			4.00				5.74				4.21	

Figure I illustrates the curing properties of two reclaims made from whole tires by the alkali process. In one case the reclaim was refined with no addition of pigment or softener on the warm-up mill and in the other case with 2 per cent of stearic acid added. The stearic acid improves the curing properties. The tensile strength is improved and the stress-strain curve indicates better reënforcing properties. The

Table III—Value of Stearic Acid in Reclaim for Activation Purposes in a Compound

	Stearic Acid Added to Compound	Stearic Acid Present in Reclaim
Smoked sheets	15	15
Reclaim, 2 per cent stearic acid	...	50
Reclaim, no stearic acid	49	...
Zinc oxide	5	5
Whiting	27.8	27.8
Sulfur	2	2
Captax	0.2	0.2
Stearic acid	1	...
	100.0	100.0

Cure at 141.6° C.	Tensile Strength		Elong.	Set	Tensile Strength		Elong.	Set
Min.	Kg./cm.²	Lbs./in.²	%	%	Kg./cm.²	Lbs./in.²	%	%
15	70.7	1007	480	33	75.5	1075	513	36
20	75.5	1074	480	35	77.6	1105	503	34
25	76.2	1085	460	33	79.4	1130	500	36
30	80.3	1142	480	36	82.4	1172	480	37
35	74.6	1062	440	33	76.9	1094	450	32
40	69.1	983	400	29	76.0	1082	437	33

per cent alkalinity as NaOH after 48 hours' extraction was 0.30 per cent on the control and 0.24 per cent when stearic acid was added.

Figure II shows two reclaims containing 10 per cent of clay added prior to refining on the warm-up mill, with 2

per cent of stearic acid added in one case. The same improvement is noted as in Figure I. Figure III gives the same comparison as Figure II, except that whiting was added instead of clay. Figure IV shows the comparison with 7.5 per cent of carbon black added.

Figure V shows a comparison of plasticity coefficients of the eight reclaims, four with and four without stearic acid. Each stock containing stearic acid is more plastic than the one without stearic acid, the difference being less marked in the stocks containing carbon black. These plasticities were run on the day following the refining operation.

Table III shows a comparison of plasticity coefficients taken a week later as against plasticities taken the day after the refining operation. The recovery results were obtained by measurement of the increase in thickness of the plasticity disk during the 10 minutes following its removal from the Williams plastometer. It is expressed as percentage increase in thickness. This result is a measure of the nerve of the reclaim. The recovery or nerve is less in the stocks in which stearic acid was used. The reduction of nerve in reclaimed rubber improves the tubing and calendering properties of compounds in which it is used. Stearic acid is valuable for this purpose because it accomplishes this result without the production of further "tack."

Effect of Stearic Acid in Compounds Containing Reclaimed Rubber

Table IV gives a comparison of physical test data of two compounds containing stearic acid. In one case stearic acid was present in the reclaim and in the other case it was added in the compound. Physical tests indicate that stearic acid present in reclaimed rubber is valuable for activation of Captax.

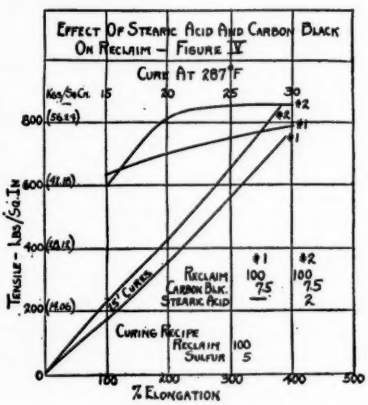
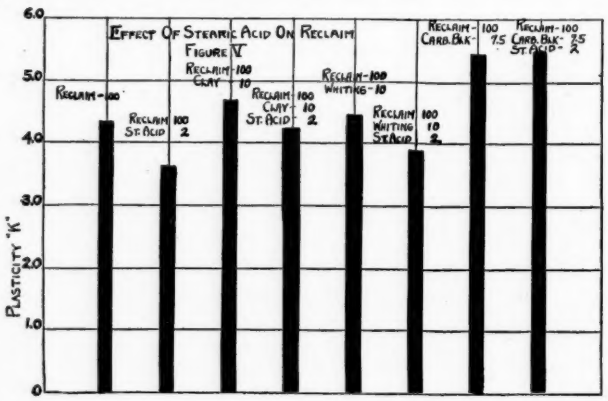


Table IV—Effect of Stearic Acid on Plasticity of Reclaimed Rubber

Stearic Acid and Pigment Added to Whole-Tire Reclaim 100	Plasticity K	Plasticity K after 1 Week	Recovery
None	4.32	4.86	4.17
Stearic acid 2	3.62	4.49	3.70
Clay 10	4.67	5.05	4.57
Clay 10, stearic acid 2	4.24	5.19	2.60
Whiting 10	4.45	4.57	3.85
Whiting 10, stearic acid 2	3.86	4.71	1.22
Carbon black 7.5	5.41	6.08	3.08
Carbon black 7.5, stearic acid 2	5.46	6.04	2.35

After plastizing, it is often desirable to add a softener on the mill to reduce excessive "tack" to metal rolls. Stearic acid reduces tack in plastic reclaims and gives stocks which have a minimum amount of nerve. They break down readily with little tendency to go to the back roll or become mushy and difficult to remove from the mill. The improvement in curing properties of reclaimed rubber produced by the addition of stearic acid indicates that the use of stearic acid in compounds containing reclaim would produce a similar improvement This has been found to be true. In compounds containing substantial amounts of alkali process reclaim, a low sulfur and a high accelerator ratio, there is sometimes a rapid reversion causing blowing after the proper cure has been reached. Compounds containing stearic acid show less



tendency to reversion under these conditions than compounds containing other softeners.

Conclusions

1—Stearic acid does not compare with other softeners in plasticizing efficiency when used in contact with vulcanized rubber scrap during devulcanization.

2—Stearic acid when added as a softener to devulcanized scrap on the mill prior to refining imparts properties which are very desirable. (*a*) Makes the reclaim batch more plastic, (*b*) improves tubing and calendering properties, (*c*) reduces nerve without production of excess tack, (*d*) improves curing properties (higher tensile strength, higher modulus, and improved molding properties) of reclaimed rubber, (*e*) when pigments are added it gives better dispersion with improved physical properties.

3—Stearic acid when used in compounds containing reclaimed rubber improves the curing properties of these compounds.

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Adsorption of Stearic Acid by Carbon

J. T. Blake

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IN A PREVIOUS paper (*1*) a new theory of pigment reenforcement was presented in which a reënforcing filler was defined as one which forms a bond with the rubber matrix that is stronger than the matrix itself. At the same time the mechanism of filler dispersion was discussed and it is the purpose of this paper to amplify that discussion.

It is well known that there are certain materials occurring naturally in raw rubber or that may be deliberately added, such as stearic acid, which are responsible for the satisfactory dispersion of fillers. Harkins' ideas on dispersions may be applied to the situation.

Plantation rubber contains approximately 2 per cent fatty acids, chiefly stearic. These fatty acids are polar compounds containing a long hydrocarbon chain and an end carboxyl group. According to Harkins this sort of material is an excellent dispersing agent. When such a dispersing agent is used in rubber, the carboxyl group is attached to the surface of the filler particle and the hydrocarbon chain is dissolved in the rubber hydrocarbon. This covers the surface of the filler particle with a monomolecular film of the dispersing agent, each molecule being rigidly oriented. The result of such an action is twofold: it separates each particle from the others by the rubber matrix and causes the matrix to adhere firmly to the surface of the filler.

By taking into account the size of the filler particles and the molecules of the dispersing agent, it is possible to calculate the amount of material required to disperse a given quantity of filler in rubber.

The dispersion of carbon black in rubber is usually incomplete when more than 30 volumes are incorporated in 100 volumes of rubber. The amount of stearic acid necessary to produce a perfect dispersion of that amount of filler is calculated to be 1.95 per cent on the rubber. There is approxi-

mately 2.2 per cent naturally occurring fatty acids in the rubber, a very good agreement with the theory.

If this is the mechanism of the dispersion, certain deductions may be made. When carbon black or any other filler is dispersed in rubber, the fatty acid is adsorbed on the filler surface; in other words, the filler is wet by the acid and not the rubber hydrocarbon. The change in heat content when a filler is mixed into rubber should therefore be the heat of wetting of the filler by fatty acid and not by the rubber hydrocarbon.

The heat of wetting of carbon by fatty acid has been found by Gaudechon (*2*) to be 6.0 calories per gram of carbon. Hock (*3*) has found the heat of wetting of carbon black by rubber to be 5.1 calories per gram of carbon at 30 volumes carbon per 100 volumes of rubber. The agreement between these figures is satisfactory, but it is desirable to check this value by an independent method.

Determination of Cohering Voltages

The determination of cohering voltages has recently attracted attention as a new method of studying adsorption. The cohering voltage of a material is the voltage required to remove an adsorbed film of it from a surface.

This cohering voltage is measured in a coherer, which consists of a glass bulb containing two touching electrodes. The electrodes may be of tungsten, platinum, or carbon. They are glowed out in a high vacuum to remove all previously adsorbed material. The material whose cohering voltage is to be measured is admitted and allowed to become adsorbed on the surface of the filament electrodes. If a low voltage is applied to them, they are found to be completely insulated from each other by the adsorbed film. A definite voltage is applied to the film by charging a condenser to this voltage from a potentiometer and connecting it to the electrodes. The junction is then tested for conductivity by means of the very low voltage of a heated thermocouple in series with a galvanometer. If increasing voltages are successively applied to the electrodes, a definite voltage is found at which the junction ceases to be an insulator and is electrically conducting. The film of material has been desorbed from the electrode surface. The applied voltage has swept off the adsorbed molecules. This critical voltage is the cohering voltage and has a definite value for each adsorbed material. It varies from a small fraction of a volt to 10 or 12 volts. Non-polar hydrocarbons, such as pentane, have very low values (0.4 volt), while water, which is a strongly polar molecule, has a value of 11 volts.

Calculation of Energy Relations of Heat of Desorption

This voltage is thus a measure of the force of adsorption of the film involved. The exact mechanism of the desorption is not known, but the energy relations may be calculated

closely. If the size of the molecules in the adsorbed film, the dielectric constant of the material, etc., are known, it becomes possible to calculate the heat of desorption. This value is of course equal and opposite in sign to the heat of adsorption.

The total heat of desorption of one mol of a substance is

$$Hm = \frac{AE^2(K-1) \times 16}{d} + L$$

where Hm = heat of desorption of one mol
A = area occupied on the surface by one mol in square centimeters multiplied by 10^{16}
E = critical or cohering voltage
K = dielectric constant of material in adsorbed film
L = molar latent heat of evaporation of material of film
d = half thickness of the film

For an oriented film the film thickness is the length of the molecule. Since in an homologous series adsorption occurs with the same chemical group, the ratio between E^2 and the length of the molecule in carbon atoms should be a constant. Palmer (*5*) has recently measured the value of this ratio for a series of fatty acids and finds it to be 4.2. For a series of alcohols the value is 4.4, implying that the adsorption is quite similar. It would seem that the active group in a fatty acid is the hydroxyl as in an alcohol. From the above relation stearic acid should have a cohering voltage of 8.9 volts, since it has an equivalent length of 19 carbon atoms.

The molar heat of vaporization may be estimated quite accurately for stearic acid at 13,930 calories by Trouton's rule. Its dielectric constant was measured in this laboratory at 1000 cycles at 25° C. and found to be 2.27. The values of A and d are given by Langmuir (*4*) as 22 and 12.5 square Ångström and Ångström units, respectively. From these values the total heat of desorption which equals the heat of adsorption is calculated to be 64.5 calories per gram of stearic acid. Using this value, it may be calculated that if rubber contains 2.2 per cent fatty acids and 30 volumes of carbon black may be successfully dispersed in 100 volumes, the heat of wetting of the carbon black by stearic acid is 4.7 calories per gram of carbon. Thus the heat of dispersion as calculated from cohering voltages checks Hock's experimental value of 5.1 calories and in turn is checked by Gaudechon's value of 6.0 calories for the wetting of carbon by acid. Additional evidence is thus given that the heat of wetting of carbon by rubber is the heat of adsorption of fatty acids by carbon. The agents that disperse carbon black in rubber are the naturally occurring fatty acids, principally stearic.

Conclusion

The equations used in the calculations are based on the assumption that the adsorbed molecules are dipoles and are adsorbed in an oriented condition. That the values check is evidence that the proposed theory of dispersion is correct and that the dispersing agent is in an oriented condition on

the surface of the filler particle. It is possible to calculate that the center of the dipole axis is 4.2 Ångströms from the filler surface. Since this value is but 20 per cent of the length of the stearic acid molecule, the carboxyl group is the chief contributor to its dipole moment. This would imply that the length of the hydrocarbon chain is probably not critical so far as the dispersing properties of a fatty acid are concerned.

The mechanism of the successful dispersion of fillers other than carbon black should be essentially the same. The whole theory throws much light on the essential part that the naturally occurring fatty acids and added stearic acid play in the dispersion of carbon black in rubber and explains why the addition of small amounts of stearic acid to rubber, especially to rubbers deficient in the naturally occurring dispersing agents, tends to produce a better and more uniform product.

Literature Cited

(1) Blake, IND. ENG. CHEM., **20**, 1084 (1928).
(2) Gaudechon, *Compt. rend.*, **157**, 209 (1913).
(3) Hock, *India Rubber J.*, **74**, 454 (1927).
(4) Langmuir, *J. Am. Chem. Soc.*, **39**, 1848 (1917).
(5) Palmer, *Proc. Roy. Soc.* (*London*), **115**, 227 (1921).

Discussion

C. R. Boggs

Doctor Blake has suggested a theory for the mechanism of filler dispersion and reënforcement. However, he deals only with carbon black in rubber. Carbon black is the most important reënforcing ingredient we have for a tire-tread compound. Being a conductor, it cannot be used in appreciable quantities in insulation. We might consider the possibility of finding a non-conducting reënforcing filler for insulation and also what should be done when the present supply of natural gas is depleted. What is needed is a material similar to clay which is cheap and has a small particle size. With present dispersing agents, clay does not, however, reënforce rubber to anywhere near the extent that carbon black does.

For a filler to reënforce satisfactorily it must be well dispersed and adhere firmly to the rubber. The correct dispersing agent should bring this about. This agent should be a polar compound. One portion of the molecule should be soluble in the rubber hydrocarbon and another portion should be capable of being adsorbed by and adhering strongly to the surface of the clay.

It would be laborious to mix clay in rubber with every material that might fulfil the above requirements for a dispersing agent and then test the product. What is needed is a relatively quick laboratory method of testing that will parallel the action of the filler in rubber. Two methods suggest themselves. The first one is that of determining the cohering voltages of various polar compounds on a clay surface. Unfortunately, clay is a non-conductor and is not adapted to use as electrodes in a coherer. The second method would consist of making a stiff paste of the filler with kerosene. The addition of a small amount of a suitable dispersing agent would thin the paste to a mobile liquid. Kerosene, being a long-chain hydrocarbon, should resemble rubber as a dispersing medium and the experiment should be analogous to the dispersion of the filler in rubber.

We have made a number of mixes of clay and kerosene and added various dispersing agents. Seventy-five per cent nitrobenzene by weight on the clay did not produce a satisfactory dispersion. Although the nitrobenzene is a strongly polar compound, no part of the molecule is apparently adsorbed by the clay. Twenty-two per cent stearic acid did produce a good dispersion, while only 2 per cent wool grease was required to reduce the stiff paste to a thin liquid. These results indicate that a small quantity of wool grease would transform clay to a strong reënforcing filler in a rubber compound. Rubber-clay compounds containing 2 per cent wool grease on the filler were mixed and cured. Their physical properties were not appreciably different from the same compounds without the wool grease. In other words, the kerosene experiment is not parallel to conditions in the rubber compound.

Present laboratory methods for examining dispersing agents are inadequate for the development of new ones and improving the ones we have now. New methods should produce materials that would do the same thing for other fillers that stearic acid does for carbon black. More theoretical work on adsorption and dispersion should develop new reënforcing fillers and be of great benefit to the rubber industry as a whole and the wire trade in particular.

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Stearic Acid in Litharge-Cured Rubber Compounds

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IT HAS been known at least since 1912 that the resins present in crude rubber are essential to vulcanization with litharge. In that year Weber (*4*) reported that deresinated rubber will not cure and concluded that "resins play an active part in the vulcanization;" but he formulated no theory of the way in which they function. At that time the composition of the rubber resins was not so well known as now. In 1916 Stevens (*3*) verified Weber's conclusions, but believed his findings supported the Esch and Auerbach (*2*) theory that litharge accelerated vulcanization through the rise in temperature occasioned by an exothermal reaction.

It is now well understood that resins promote vulcanization through their content of organic acid. It was proposed by Bedford and Winkelmann (*1*) in 1924 that litharge vulcanization proceeds by the following steps: (*a*) reaction of lead oxide with an organic acid (naturally present in the resin or added during the mixing) to form a rubber-soluble soap; (*b*) reaction of the lead soap with hydrogen sulfide to form a hydrosulfide salt or a hydrosulfide; (*c*) reaction of the latter with sulfur to form a disulfide and then a polysulfide; (*d*) decomposition of the (unstable) polysulfide to yield a very active form of sulfur—the ultimate vulcanizer. The polysulfide theory has been generally accepted as accounting adequately for the known facts.

It is clear, then, that the efficiency of litharge as an accelerator is absolutely dependent upon the existence of an organic acid in the rubber as mixed. The mere statement of this general principle, however, by no means gives the compounder all the information he desires in the matter of organic acids as related to litharge curing. Various questions of practical importance arise. In the present paper an attempt will be made not comprehensively or systematically to survey all these numerous questions, but only to illustrate a number of scattered but specific cases. It is advisable not to gen-

eralize too broadly, but to confine the conclusions to the particular conditions applying to each case.

Low-Grade and High-Grade Crude Rubbers—High Zinc Oxide Stock

Several years ago the writer made a study of various softeners in a high zinc oxide litharge compound, using the formula:

Rubber	100
Sulfur	8
Litharge	20
Zinc oxide	100
Softener	5

Two series of stocks were made up, one using a typical "high-grade" crude (smoked sheet) and the other a "low-grade" wild rubber (Lapori). Each series was master-batched up to the point of adding the various softeners, which were added to portions of the master batches on the laboratory mill. The stocks were vulcanized in the press at 141° C. (40 pounds steam) over a series of cures in order adequately to develop the optimum cure and to show the effect of the various softeners on the two grades of rubber. Stress-strains were determined on all the vulcanizates.

The results were entirely different for the two crudes, as will be seen from Tables I and II. In Table I the physical properties of the stocks of the Lapori series at their optimum cures (defined by maximum energy) are shown. While the control mix (without softener) came to an optimum in 150 minutes with a tensile of 2115 pounds per square inch, most of the softeners reduced the time to reach optimum and raised the properties at optimum. This table should not be used to draw fine distinctions between two given softeners, particularly where they are close together in the table. But the outstanding fact is that those softeners which are either acids or salts, or contain an acid, and which therefore can bring the lead into solution in the rubber as a salt, are the ones which significantly aided the cure.

On the other hand, in the corresponding data for the smoked sheet series we find no enhancement of cure by any of the softeners. As measured by time to reach optimum and (or) properties at optimum, most of the softeners inflicted some damage (slight or moderate). It should be noted, however, that this damage in the case of smoked sheet is distinctly less than the benefit conferred by the acid class of softeners on Lapori.

A further insight into the results themselves is furnished by Table II, giving the stress-strains for all the cures on both Lapori and smoked sheet compounded without and with 5 per cent stearic acid. The data for Lapori emphasize how far apart in their properties the control stock and the stearic acid stock are at a given cure. For example, on this basis stearic acid about doubled the modulus of Lapori. The presence of bloom up to 180 minutes without stearic and its

disappearance between 60 and 90 minutes with stearic further confirm the accelerating effect of this acid.

In sharp contrast to these are the results on smoked sheet. Here there is, if anything, a retardation of cure by stearic and at a given cure the modulus is greatly lowered, although the tensile is not much affected. This serves to emphasize that the observed stiffening of the Lapori vulcanizate is the net result of two opposing tendencies: (*a*) a stiffening due to the enhancement of the cure, consequent in turn upon the acid bringing more lead into the available, soluble form; (*b*) a softening quite analogous to that of any non-acidic softener such as mineral oil or mineral rubber. What the net result will be in a given case depends upon the magnitude of the two component effects. Where, as in many low-grade crudes, the natural resin content is low or deficient in acid, an addition of stearic acid, oleic acid, pine tar, or similar

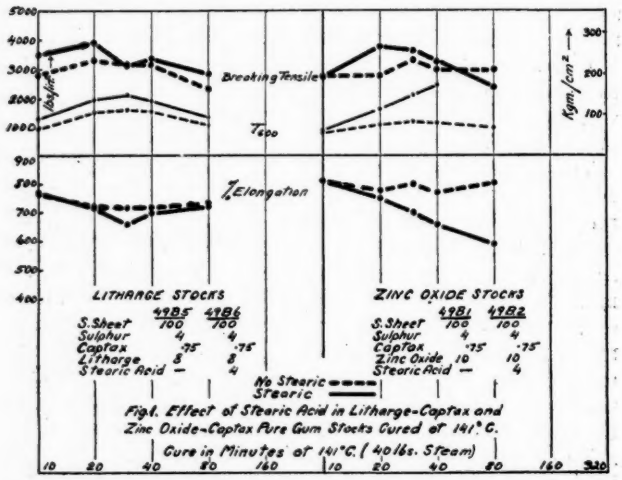

Fig1. Effect of Stearic Acid in Litharge-Captax and Zinc Oxide-Captax Pure Gum Stocks Cured at 141° C.

material greatly accelerates otherwise slow curing and enhances otherwise low properties; on the other hand, where the natural acid content is relatively high, a further addition shortens the time of cure little or none (it may retard) and the resulting observed effect is likely to be a distinct softening at a given cure.

The effect of the softeners on set should be noted. This was measured on specimens broken in the course of determining stress-strains and was taken from 5 to 10 seconds after the break. With few exceptions set was increased by the softeners, this being true for both grades of rubber but more marked with smoked sheet. This phenomenon is doubtless closely allied to softening action, both being expressions of the reduction of elastic properties. Hardwood pitch—which, however, only moderately enhanced the curing of Lapori—in the case of both grades of crude had about the least effect on set.

There is little doubt in the writer's mind that a smaller quantity of softener than used throughout the present series would, in the case of the more active ones at least, have furnished maximum activation. It is clear that it is useless to go beyond a certain limit which, in so far as curing considerations are concerned, is perhaps nil for standard smoked sheet and for the present type of formula. In the case of Lapori, perhaps from 2 to 3 per cent of stearic acid would have yielded maximum activation. To exceed the limit for full activation means to increase the softening action on the vulcanizate.

Stearic Acid in a Pure Gum and a Gas Black Stock

In the remaining cases we are dealing with smoked sheet, which normally does not require an addition of acid in so far as enhancement of cure with litharge is concerned. Tables III and IV illustrate this, Table III showing results for a pure

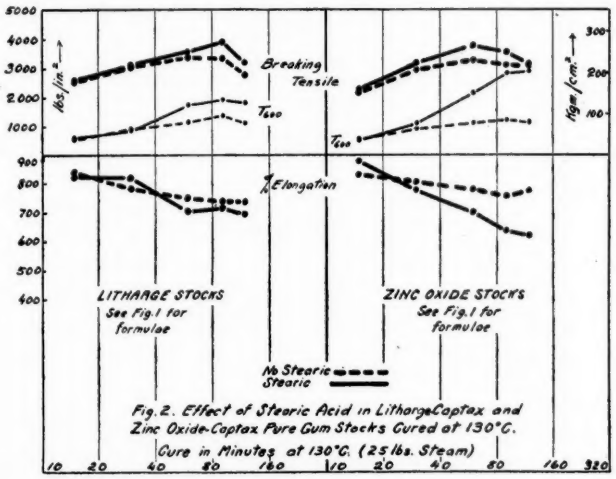

Fig. 2. Effect of Stearic Acid in Litharge-Captax and Zinc Oxide-Captax Pure Gum Stocks Cured at 130°C.

gum mix and Table IV for a gas black stock. The pure gum stock (49A2) with 1 per cent of stearic acid follows closely in its properties that with no added acid (49A1), and has an identical rate of cure. There is a very slight softening effect on the part of the stearic.

With gas black stearic improved the tensile significantly. As the object was to determine not the dispersing action of the stearic on the black, but rather the effect on curing, the softener was so added as to minimize any benefit it might confer on dispersion; i. e., the rubber, sulfur, black, and litharge were master-batched and 4 per cent stearic was subsequently milled into half of this batch to yield 49A5. There is meager, and only meager, evidence of enhancement of cure by the stearic. The increase in tensile at all cures, on the other hand, is distinct; it is due to increased elonga-

Table I—Physical Data for Cures of Maximum Resilient Energy of Litharge-Rubber Stocks Activated with Various Softeners. Cured in Press at 141° C. (40 Pounds Steam)

Softener	Cure of Max. Energy	Tensile at Elongation of:		Tensile	Elong.	Supermanent Set	T. P.	Energy
		300%	600%					
	Min.	*Lbs./sq. in.*		*Lbs./sq. in.*	*%*	*%*		*Ft-lbs./cu. in.*
				Litharge–Lapori Stock				
Rubberite	30	455	2327	3200	685	51	219	546
Benzoic acid	30	445	2270	2660	640	36	170	433
Rosin	60	395	2090	3252	705	54	229	542
Zinc stearate	60	475	2310	3000	670	53	200	510
Pine tar	60	477	2585	3067	645	48	198	499
Rosin oil	60	495	2625	2875	630	46	181	464
Zinc benzoate	60	585	2790	2817	605	46	170	457
Oleic acid	60	480	2542	2850	630	52	180	446
Stearic acid	60	450	2312	2622	635	44	166	419
Phenol	90	642	2267	2535	650	38	164	493
Hardwood pitch	90	537	2030	2232	630	32	141	405
Lead phenolate	90	417	1545	2142	675	42	144	382
Cumar, grade 310	90	305	1157	1760	705	35	124	323
n-Butyl salicylate	90	347	1365	1837	670	32	123	320
Glycerol	120	195	730	1150	705	38	81	208
Nil (control)	150	487	1695	2115	655	29	138	387
Cumar, grade 315	150	397	1367	1540	640	31	95	291
Cumar, varnish grade	> 150	482	1640	1890	640	33	121	357

LITHARGE–SMOKED SHEET STOCK

Nil (control)	15	562	2970	3567	665	36	237	635
Hardwood pitch	15	627	2977	3355	655	31	220	620
Cumar, grade 310	15	530	2850	3427	660	37	226	590
Cumar, varnish grade	15	517	2782	3347	660	37	221	574
Zinc stearate	20	420	2242	3762	730	54	275	660
n-Butyl salicylate	20	577	2795	3385	670	35	226	622
Lead phenolate	30	1085		3542	590	45	209	645
Cumar, grade 315	30	675	3062	3670	650	49	239	634
Oleic acid	30	753	3565	3665	610	52	223	610
Phenol	30	902	3527	3527	600	43	212	608
Rubberite	30	740	3280	3510	620	42	218	601
Zinc benzoate	30	655	3102	3462	630	42	218	579
Rosin oil	30	730	3192	3360	615	42	206	567
Stearic acid	30	580	3067	3430	635	52	217	564
Benzoic acid	30	620	3240	3540	620	42	219	562
Glycerol	30	560	2480	3015	650	49	198	510
Pine tar	45	718	3075	3725	650	46	242	654
Rosin	45	715	3220	3485	625	44	217	597

Conversion factor for tensiles: 1 lb. per sq. in. = 0.0703 kg. per sq. cm.
Conversion factor for energies: 1 ft-lb. per cu. in. = 0.84 kg-cm. per cc.

Table II—Effect of 5 Per Cent Stearic Acid in Litharge Stock Loaded with Zinc Oxide

Cure at 141° C.	Tensile at Elongation of:								Tensile	Elong.	Subpermanent Set	T. P.	Energy	Bloom[a]
	100%	200%	300%	400%	500%	600%	700%	800%						
Min.	*Lbs./sq. in.*								*Lbs./sq. in.*	%	%	*Ft-lbs./cu. in.*		
LAPORI WITH NO STEARIC ACID														
60	85	150	235	350	595	1000	1520		1595	715	32	114	284	+
90	94	165	282	420	700	1062			1625	690	24	112	283	+
120	107	222	372	555	920	1402			1872	670	25	125	335	+
150	137	300	487	740	1090	1695			2115	655	29	138	387	+
180	145	280	465	692	1062	1652			2000	650	27	130	365	+
LAPORI WITH 5 PER CENT STEARIC ACID														
30	137	212	320	520	1022	1935			2702	675	45	182	410	+
60	192	300	450	717	1347	2312			2622	635	44	166	419	+
90	232	367	520	837	1477				2050	565	40	116	320	−
SMOKED SHEET WITH NO STEARIC ACID														
10	105	257	425	767	1407	2395			3180	675	36	214	521	
15	167	332	562	1065	1880	2970			3567	665	36	237	635	
20	197	400	652	1107	1940	2992			3572	655	39	234	633	
SMOKED SHEET WITH 5 PER CENT STEARIC ACID														
10	85	130	202	320	575	1110	1922	2922	3140	825	51	259	547	
15	157	210	335	570	1117	1982	3055		3135	710	45	222	517	
20	165	270	397	645	1272	2222	3365		3365	700	48	235	554	
30	238	385	580	1025	1868	3067			3430	635	52	217	564	
45	277	430	665	1113	1970	3040			3040	600	53	182	498	

[a] A plus sign (+) means sulfur bloom present, a minus sign (−) means bloom absent.

tion (not stiffness), and probably represents improved dispersion, notwithstanding the precaution to the contrary.

Why have we only a slight softening of the gas black stock by 4 per cent stearic (assuming that the softening exhibited by Table IV is significant at all), while in Table II for smoked sheet 5 per cent stearic cut the modulus in half; and why with the black have we evidence of (slight) activation of cure but with zinc oxide appreciable retardation by the stearic added? Two possible explanations suggest themselves: (1) With gas black an appreciable part of the stearic may be adsorbed, leaving only the free part to soften the rubber phase. If this is the case, then conceivably there was a moderate deficiency of free organic acid in 49A4 which was made up in 49A5 by the added acid. A much smaller adsorptive effect is to be expected from the zinc oxide. (2) Probably the dispersion of the black was improved by the stearic, introducing thus a stiffening factor which would operate against the softening action of the stearic on the rubber phase. If so, with zinc oxide there would be no corresponding stiffening factor consequent upon improved dispersion and higher reënforcement, since zinc oxide disperses readily without added stearic.

Stearic Acid and Litharge in Conjunction with Mercaptobenzothiazole

The observations made above are on stearic acid in stocks accelerated by litharge. It is of interest to note what obtains when litharge is used in conjunction with an organic accelerator as an "activator," analogously to zinc oxide. For this purpose mercaptobenzothiazole (Captax) was employed, since (*a*) litharge strongly activates this accelerator and (*b*) it is well known that when zinc oxide is used as the activator a full curing propensity is highly dependent on stearic acid, especially in the presence of gas black.

Two base stocks were master-batched:

Pure Gum Base		Gas Black Base	
Smoked sheet	100	Smoked sheet	100
Sulfur	4	Sulfur	4
Captax	0.75	Captax	0.75
		Gas black	45

Each stock was then subdivided into four parts each and to these portions the following additions were made:

Litharge	8
Litharge Stearic acid	8 4
Zinc oxide	10
Zinc oxide Stearic acid	10 4

Thus there were studied all the combinations which arise from varying the following items:

Reënforcement (and concomitant adsorptive effects)	Pure gum *vs.* high gas black
Activation	Litharge *vs.* zinc oxide
Acidic softener (added)	Stearic absent *vs.* stearic present

Table III—Effect of 1 Per Cent Stearic Acid in a Pure Gum Litharge Stock

	Formulas	
	49A1	49A2
Smoked sheet	100	100
Sulfur	5	5
Litharge	15	15
Stearic acid	...	1

Cure at 141° C.	Tensile at Elongation of:								Tensile	Elong.	T. P.	Energy
	100%	200%	300%	400%	500%	600%	700%	800%				
Min.	*Lbs./sq. in.*								*Lbs./sq. in.*	*%*		*Ft-lbs./cu. in.*
	49A1—NO STEARIC ACID											
10	64	86	128	214	343	621	1220	2135	2135	800	171	312
20	65	119	195	303	541	1090	2110		2895	765	222	416
30	86	150	237	387	667	1290	2580		3120	755	236	473
40	90	157	290	470	883	1690			2840	695	197	407
80	90	156	279	458	727	1340	2390		2435	705	172	364
	49A2—1 PER CENT STEARIC ACID											
10	66	88	154	220	341	637	1230	2175	2195	805	177	326
20	66	109	174	304	511	1045	2055		2830	760	215	375
30	87	152	238	335	606	1230	2490		3075	740	228	417
40	85	171	299	499	792	1645	2890		2890	700	202	411
80	65	139	286	408	667	1265	2365		2450	720	176	374

Table IV—Effect of 4 Per Cent Stearic Acid in a Gas Black Litharge Stock

Formulas	49A4	49A5
Smoked sheet	100	100
Sulfur	5	5
Litharge	15	15
Gas black	45	45
Stearic acid	...	4

Cure at 141° C.	Tensile at Elongation of:							Tensile	Elong.	T. P.	Energy
	100%	200%	300%	400%	500%	600%	700%				
Min.	*Lbs./sq. in.*							*Lbs./sq. in.*	*%*		*Ft-lbs./cu. in.*
	49A4—NO STEARIC ACID										
10	128	330	771	1430	2240	3140		3450	645	223	663
15	183	438	1035	1790	2755	3725		3890	610	237	704
20	264	622	1360	2260	3385	4285		4360	610	265	872
30	336	822	1610	2485	3625			4225	560	237	785
40	444	981	1850	2780	3835			4350	550	239	835
60	430	1050	1970	3040	4035			4035	500	202	709
80	490	1155	2080	3195				3980	475	189	668
	49A5—4 PER CENT STEARIC ACID										
10	121	282	684	1295	2110	2975	3900	4060	715	291	834
15	157	395	880	1585	2540	3480	4485	4485	700	314	940
20	233	602	1240	2060	3070	4100		4520	640	290	915
30	322	798	1640	2610	3745			4460	570	254	843
40	414	1005	2030	3035	4140			4550	545	248	877
60	505	1315	2160	3320				4265	485	207	739
80	424	1110	1930	3030	4145			4145	500	207	718

Table V—Effect of Stearic Acid on Litharge-Captax and Zinc Oxide–Captax Pure Gum Stocks, Cured at 141° C. (40 Pounds Steam)

Cure	Tensile at Elongation of:								Tensile	Elong.	T. P.	Energy
	100%	200%	300%	400%	500%	600%	700%	800%				
Min.	*Lbs./sq. in.*								*Lbs./sq. in.*	*%*		*Ft lbs./cu. in.*
						49B5—8 PER CENT LITHARGE, NO STEARIC ACID						
10	64	115	158	285	495	947	1960		2800	765	214	381
20	82	142	244	406	670	1500	2800		3300	725	239	435
30	83	144	248	433	742	1600	2900		3150	715	225	427
40	96	135	250	425	750	1540	2850		3150	720	227	435
80	79	128	227	345	582	1045	1960		2320	735	171	344
						49B6—8 PER CENT LITHARGE, 4 PER CENT STEARIC ACID						
10	85	128	223	330	617	1275	2390		3490	770	269	493
20	85	180	298	489	900	1950	3600		3900	715	279	522
30	123	204	337	531	1000	2100			3100	660	205	400
40	89	203	334	527	925	1900	3350		3350	700	235	471
80	79	158	276	423	710	1340	2480		2835	725	206	407
						49B1—10 PER CENT ZINC OXIDE, NO STEARIC ACID						
10	66	99	154	253	450	792	1515	2705	2745	810	222	413
20	89	125	206	331	572	1050	1950		2800	780	218	437
30	68	135	225	360	600	1140	2100	3300	3300	800	264	523
40	63	157	241	380	600	1120	2050		2995	770	231	446
80	64	127	212	339	581	953	1715	2920	2965	805	239	466
						49B2—10 PER CENT ZINC OXIDE, 4 PER CENT STEARIC ACID						
10	70	93	163	279	465	860	1615	2600	2720	810	220	426
20	92	161	253	402	758	1605	2870		3750	750	281	531
30	93	185	324	566	1040	2080	3610		3610	700	253	508
40	114	239	432	682	1270	2450			3250	660	215	473
80	106	212	405	681	1300				2380	590	140	309

It will be noted that here, as in an earlier experiment, the stearic was added after the milling of the gas black into the gum, in order to influence dispersion in a minimal way. These eight stocks were then press-cured over a range at 141° C. (40 pounds steam) and at 130° C. (25 pounds steam) and stress-strains were determined on all vulcanizates.

The complete physical data including tensile product (T. P.) and energy are displayed in Tables V to VIII, and certain of these data are, for readier assimilation, graphed in Figures 1 to 4. In the graphs will be found breaking tensiles, elongations, and moduli, the latter being represented by tensiles at 600 per cent elongation (T_{600}) for pure gum stocks and at 400 per cent elongation (T_{400}) for gas black stocks. Each graph is based directly on one of the tables—for example, Figure 1 on Table V, 2 on VI, etc. The curves obtained with and without stearic acid (other conditions being constant) are superimposed in the same space (stearic present

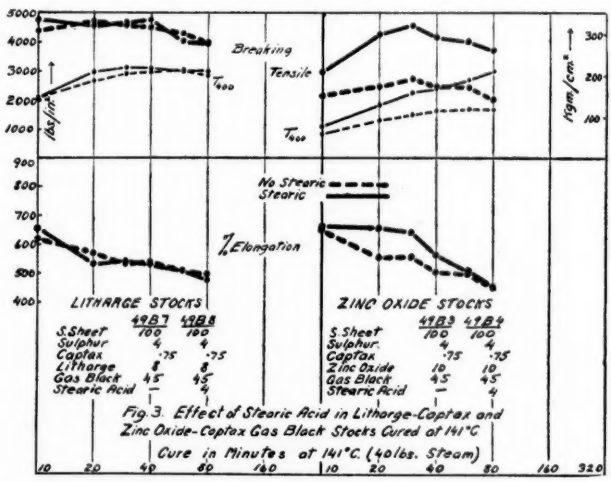

Fig. 3. Effect of Stearic Acid in Litharge-Captax and Zinc Oxide-Captax Gas Black Stocks Cured at 141°C

represented by solid lines, stearic absent by broken lines). In this way the effect of stearic acid in a given set of conditions is observable at a glance. In reading the graphs due account of the logarithmic time scale should be taken.

The outstanding result is that the behavior of the litharge-Captax combination toward stearic acid is in sharp contrast to that of the zinc oxide–Captax combination. The former is seen to be relatively independent of added stearic for its activity, coming to approximately full properties without the acid; the latter is highly dependent on, and produces its maximum results only with, added acid. These general conclusions hold for both the pure gum and the gas black stocks, though more pronounced for the black.

Examining the graphs in detail we find as follows: In Figure 1 (pure gum mixes cured at 141° C.), in the case of litharge

Table VI—Effect of Stearic Acid on Litharge-Captax and Zinc Oxide–Captax Pure Gum Stocks, Cured at 130° C. (25 Pounds Steam)

Cure	Tensile at Elongation of:								Tensile	Elong.	T. P.	Energy
	100%	200%	300%	400%	500%	600%	700%	800%				
Min.	*Lbs./sq. in.*								*Lbs./sq. in.*	*%*		*Ft-lbs./cu. in.*
49B5—8 per cent litharge, no stearic acid												
15	48	72	120	169	313	566	1095	2075	2555	840	215	362
30	72	119	167	286	452	906	1980		3050	785	240	427
60	68	137	205	319	557	1145	2265		3390	750	254	415
90	88	142	230	394	689	1380	2690		3370	740	249	457
120	74	128	214	363	599	1095	2375		2780	735	204	380
49B6—8 per cent litharge, 4 per cent stearic acid												
15	66	88	131	219	339	612	1245	2175	2600	825	214	365
30	83	124	187	280	457	861	1765	2700	3110	820	255	474
60	95	167	286	443	822	1735	3515		3570	705	247	457
90	82	174	298	432	893	1905	3610		3900	715	279	513
120	97	146	267	473	837	1805			3200	695	222	425
49B1—10 per cent zinc oxide, no stearic acid												
15	51	76	101	164	304	557	1035	1845	2155	830	179	317
30	73	97	170	291	485	896	1780	2905	2930	805	236	449
60	66	131	219	339	558	1085	2100		3260	780	254	466
90	89	134	223	400	656	1220	2355		3110	755	235	450
120	74	148	245	393	664	1140	2260		3075	775	238	483
49B2—10 per cent zinc oxide, 4 per cent stearic acid												
15	48	72	96	169	277	506	933	1555	2290	880	202	368
30	67	123	202	290	548	1085	2010		3175	775	246	439
60	97	193	338	554	1020	2170	3740		3740	700	262	520
90	116	232	419	709	1425	2840			3535	635	225	453
120	129	269	456	773	1590	2900			3155	620	196	439

the tensile and modulus are appreciably raised by stearic acid but the properties as a whole are not changed so radically as in the case of zinc oxide. With the latter we have an otherwise low modulus greatly raised and an otherwise high elongation considerably lessened, especially in the longer cures. These two effects on modulus and stretch influence the tensile oppositely so that it has not undergone any more change than it did with litharge. Notwithstanding the near-identity in the influence of stearic acid on breaking tensile in the case of the pure gum litharge and pure gum zinc oxide stocks, the dependence of modulus and elongation in the case of zinc oxide constitutes a difference in vulcanizing behavior which is significant from the practical standpoint certainly, and from the theoretical perhaps. Figure 2, displaying properties on the same four stocks as Figure 1, but cured at 131° C., leads to the same conclusions.

The conclusion, discernible on analysis of the pure gum

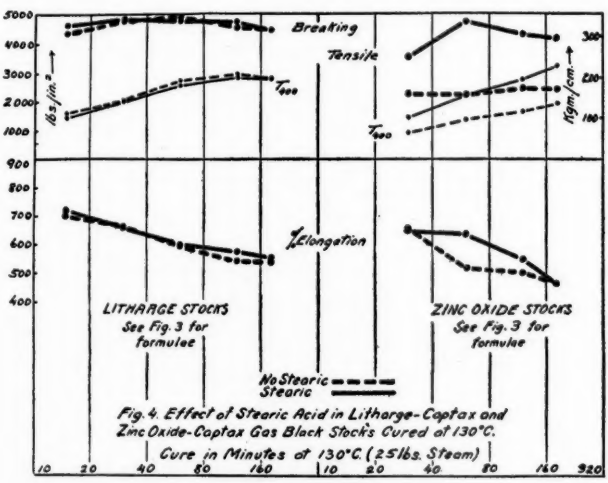

Fig. 4. Effect of Stearic Acid in Litharge-Captax and Zinc Oxide-Captax Gas Black Stocks Cured at 130°C.

results, that there is a significant difference in the behavior toward stearic acid of litharge-Captax and of zinc oxide–Captax stocks, is confirmed by the data for the gas black mixes. Both Figure 3 (141° C. cures on gas black stocks) and Figure 4 (130° C. cures) show an almost complete lack of influence by added stearic when litharge is used for activation but a marked dependence on the acid when zinc oxide is used. For example, at 141° C. either with or without stearic, the litharge-activated stocks reached a tensile of 4400 to 4700 early in the cure and maintained this value approximately unchanged to the 40-minute cure. On the other hand, while the zinc oxide stock with stearic showed a maximum tensile of 4540 reached in the 30-minute cure, without stearic only 2750 was reached (also in 30 minutes). Similarly, at 130° C. the litharge stocks, with or without

Table VII—Effect of Stearic Acid on Litharge-Captax and Zinc Oxide–Captax Gas Black Stocks, Cured at 141° C. (40 Pounds Steam)

Cure	Tensile at Elongation of:						Tensile	Elong.	T. P.	Energy
	100%	200%	300%	400%	500%	600%				
Min.	*Lbs./sq. in.*						*Lbs./sq. in.*	*%*		*Ft-lbs./cu. in.*
49B7—8 PER CENT LITHARGE, NO STEARIC ACID										
10	215	503	1077	2095	3085	4100	4395	620	273	823
20	297	737	1585	2660	3800		4710	570	269	843
30	345	864	1780	2910	4040		4565	535	245	785
40	364	892	1830	2980	4100		4500	540	243	820
60	349	923	1860	3010	4170		4290	510	219	721
80	324	838	1740	2865	3930		3930	500	197	645
49B8—8 PER CENT LITHARGE, 4 PER CENT STEARIC ACID										
10	236	549	1175	2060	3100	4160	4750	655	311	971
20	305	876	1790	2970	4150		4530	530	240	777
30	345	934	1970	3120	4305		4670	545	255	878
40	352	957	1900	3075	4200		4755	530	252	811
60	350	941	1850	3025	3980		4020	510	205	713
80	350	914	1850	2995			3900	480	187	614
49B3—10 PER CENT ZINC OXIDE, NO STEARIC ACID										
10	90	233	466	834	1345	1880	2135	650	139	409
20	156	390	750	1300	2000		2475	555	137	402
30	191	450	850	1500	2250		2750	560	154	468
40	209	490	969	1645	2440		2480	505	125	388
60	267	554	985	1720	2465		2465	500	123	397
80	280	561	1040	1700			2035	455	93	313
49B4—10 PER CENT ZINC OXIDE, 4 PER CENT STEARIC ACID										
10	123	288	586	1095	1740	2460	2975	665	198	569
20	234	566	1085	1840	2800	3765	4270	655	280	885
30	318	723	1355	2260	3310	4385	4540	625	284	939
40	400	830	1505	2405	3505		4150	565	234	765
60	408	929	1735	2695	3775		4020	510	205	670
80	457	1105	1980	2980			3700	450	167	558

Table VIII—Effect of Stearic Acid on Litharge-Captax and Zinc Oxide–Captax Gas Black Stocks, Cured at 130° C. (25 Pounds Steam)

Cure	Tensile at Elongation of:							Tensile	Elong.	T. P.	Energy
	100%	200%	300%	400%	500%	600%	700%				
Min.	*Lbs./sq. in.*							*Lbs./sq. in.*	*%*		*Ft-lbs./cu. in.*
49B7—8 PER CENT LITHARGE, NO STEARIC ACID											
15	159	375	827	1590	2460	3380	4370	4370	700	306	915
30	224	576	1200	2120	3105	4200		4815	665	320	1021
60	290	791	1670	2720	3905			4885	595	291	967
120	376	959	1875	2935	4070			4520	545	246	843
180	352	868	1745	2825	4000			4450	540	240	790
49B8—8 PER CENT LITHARGE, 4 PER CENT STEARIC ACID											
15	146	376	794	1445	2380	3310	4385	4640	720	334	962
30	217	578	1125	1995	2980	4120		4870	660	321	971
60	287	772	1542	2560	3700	4740		4740	600	285	936
120	370	970	1845	2840	3970			4725	575	272	939
180	365	942	1805	2810	3900			4445	555	247	847
49B3—10 PER CENT ZINC OXIDE, NO STEARIC ACID											
15	Very porous										
30	115	253	518	892	1480	1985		2265	655	148	452
60	187	453	825	1370	2000			2215	520	116	355
120	230	570	1020	1650	2400			2440	505	123	399
180	330	725	1210	1910				2425	465	113	386
49B4—10 PER CENT ZINC OXIDE, 4 PER CENT STEARIC ACID											
15	Porous										
30	159	398	829	1455	2170	2995		3525	650	229	678
60	279	690	1320	2180	3180	4310		4710	635	299	948
120	415	979	1765	2755	3905			4280	550	235	826
180	515	1130	2085	3215				4140	465	193	644

stearic, maintained a tensile of approximately 4400 to 4900 over the curing range of 15 to 180 minutes. With zinc oxide and stearic a maximum of 4710 was reached in 60 minutes, but without stearic a maximum of only 2440 was reached (in 120 minutes).

There is obviously some, at least quantitative, difference in the mechanism of mercaptobenzothiazole acceleration in conjunction with the two oxide activators, a difference which is accentuated when to the gum there is added an agent which powerfully adsorbs the organic acid and (or) the accelerator. Of what this difference in mechanism consists we shall not attempt to say. Possibly it has to do with the extent to which lead and zinc, respectively, are made available to the mercaptan so as to permit of mercaptide formation, this in turn being influenced by the solubilities or mobilities of lead stearate and of zinc stearate; or, on the other hand it might have to do with a difference in the chemistry of the lead and of the zinc mercaptides after their formation.

From the practical standpoint, a compound formulated along the line of 49B7 offers desirable qualities as a tread stock including high physical properties maintained over a wide range of cures. This sort of compound would appear also to be adapted to the present-day tendency toward low-temperature cures, with the advantage which that practice has of minimizing the damage to the rubber by heat. Because the litharge-Captax tread stock cures fully without the addition of stearic acid, it is not to be inferred that none should be added. That depends on requirements other than curing which may demand this ingredient, including obtaining a proper dispersion of the black and a desirable plasticity for tubing or calendering. But the point is that the stearic can be regulated in whatever way satisfies these other considerations with the assurance that curing requirements will have been met incidentally. Possibly in this way the amount of stearic used in general practice in a tread could be reduced, resulting in a lessened tendency toward stearic acid blooming.

Summary

Although an organic acid is essential to vulcanization with litharge, smoked sheet usually has enough natural acid for full activation. For example, when 5 per cent stearic acid (or similar softeners) was added to a standard smoked sheet in a high zinc oxide stock the properties were lowered. On the other hand, a "low-grade" rubber, Lapori, was greatly improved in a high zinc oxide formula by stearic and by other acids.

Acidic softeners in a high zinc oxide stock increased set, even when they promoted vulcanization.

In a pure gum litharge formula with smoked sheet, 1 per cent stearic had but little effect, while in a high gas black formula, 4 per cent stearic raised the tensile (probably due to

improved dispersion) but had no marked effect on rate of cure.

When litharge was used as the activator for mercaptobenzothiazole, stearic acid had but little effect either in pure gum or high gas black stocks. On the contrary, when zinc oxide was used proper curing was highly dependent on stearic, especially with gas black. The litharge-mercaptobenzothiazole compounds with gas black in tread stock proportions, either with or without stearic, yielded a high tensile over a wide range of cures.

Acknowledgment

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Literature Cited

(1) Bedford and Winkelmann, IND. ENG. CHEM., **16**, 32 (1924).
(2) Esch and Auerbach, *Gummi-Markt*, **1911**, 123.
(3) Stevens, *J. Soc. Chem. Ind.*, **35**, 874 (1916).
(4) Weber, *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, **9**, 95 (1912).

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Dispersion of Pigments in Rubber—II[1]

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A theoretical conception of the reënforcement of rubber by pigments has been developed.

New experimental evidence has been presented which leads to a better understanding of the final dispersion and reënforcement of a rubber compound. It is shown that pigment reënforcement is influenced by (*a*) rubber structure, (*b*) the state of aggregation of proteins and natural resins, (*c*) the isotropic properties of carbon-black particles, and (*d*) the presence of recrystallized rhombic sulfur at the beginning of vulcanization.

A PREVIOUS paper (*10*)* described the distribution of particles in compounded rubber with special reference to agglomeration and flocculation. It was emphasized that a correct understanding of the final dispersion and reënforcement of a rubber compound could only be obtained with a more thorough knowledge of the structure and physical-chemical properties of rubber and pigments themselves and of the nature of the vulcanization process. New experimental results in regard to these particular points are presented in the following investigation.

Theoretical

Owing to lack of agreement in regard to terminology, a number of conceptions considered in this paper will first be defined and discussed from a rubber-compounding point of view.

Surface energy or tension, free surface energy, interfacial

[1] Presented before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

* Italic numbers in parenthesis refer to literature cited at end of article.

tension is the specific attraction existing at a surface. On account of the unsymmetrical field of force surrounding molecules at a surface, the molecules adjust themselves in such manner as to give a surface of minimum potential energy. It is evident that energy must be added to a system of rubber and undispersed pigment if additional rubber and pigment surface or interface between rubber and pigment is to be formed. The greatest part of this energy is added in form of work. Since the work may be given back in contraction of the surface, this amount of energy is said to be preserved in the surface as free energy. Interfacial tension is a measure of the amount of free energy present in the interface.

Wetting, adhesion tension, attraction (between rubber and pigment) is the decrease in free surface energy taking place

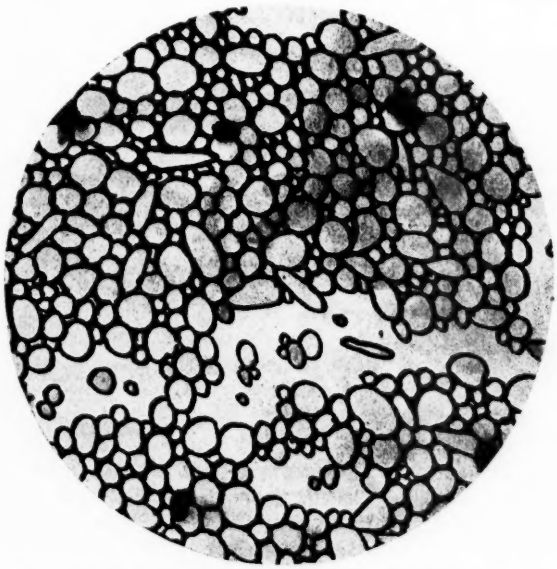

Figure 1—No Breakdown. Microscopical Drawing Approximately 5000 ×

when a rubber surface is brought in contact with a pigment surface forming an interface.

Change in the distribution of pigments in a system rubber-pigment before reaching a state of equilibrium and a final degree of dispersion can be classified as follows: (1) aggregation—by (*a*) agglomeration or (*b*) flocculation; (2) disaggregation (dispersion)—by (*a*) disagglomeration or (*b*) deflocculation. (*a*) is the tendency of unwetted particles to group or spread, whereas (*b*) is the same tendency of wetted particles. These changes can take place during the milling operations as well as during vulcanization.

Different types of particles are encountered before final dispersion is obtained in a rubber compound—primary particles,

the size and shape of which are regulated by the molecular forces of cohesion; secondary particles, those formed as a result of aggregation from primary particles.

Relation between wetting, interfacial tension, and dispersion. Dispersing agents known in rubber compounding are substances that reduce the interfacial tension between the pigment particle and the rubber. The smaller the interfacial tension the greater will be the attraction between the filler and the rubber. The intensity of the wetting or adhesion tension regulates the tendency to aggregation and consequently the dispersion.

Both physical and chemical changes at the surface of the pigment particles may take place during milling and vulcanization which would influence the interfacial tension and cause changes in the permanent dispersion of the particles. That chemical changes actually occur at the surface of certain pigment particles during vulcanization has been shown by Pohle (*22*).

On the other hand, Wiegand (*29*) points out that dispersing agents may profoundly affect the consistency of the rubber phase and that proper dispersion cannot take place when the viscosity of the rubber falls below a certain point. According to Hauser (*12*), certain pigments reach a maximum dispersion during milling followed by aggregation when the mastication is continued. The consistency of rubber is influenced not only by mastication and softeners, but also by various compounding ingredients, such as accelerators, antioxidants, and certain dry powders. The powders have been studied in detail by Hurlston (*17*). Finally, the application of heat and the action of sulfur during vulcanization produce the most pronounced changes in the consistency and strength of the rubber phase.

According to theoretical considerations developed by Bartell and Osterhof (*1*) and experimental work by Hock (*14*) and others, different pigments would be wetted to different degree by the rubber, the wetting power being specific in its relation to a certain pigment. The wetting power would be a function not only of the surface energy of the rubber, but also of the specific attractions operating between the filler and the rubber at the interface. In rubber compounding the pigments to a great extent are forcibly inserted in the rubber by mechanical means and the pigment becomes wetted by the rubber to a certain definite degree, this being dependent upon the magnitude of the decrease in free surface energy. During the milling large amounts of free surface energy are developed and the surface of the rubber is brought in contact with that of the filler. The free surface energy of the interface is then more or less rapidly decreased by the specific forces in the filler and the rubber acting upon each other and wetting is procured. This may take place instantaneously or it may vary with the accumulation of surface-active substance in the interface. The point in the processing at which maximum

wetting occurs is not known. The degree of wetting seems to be low during milling and during the first part of vulcanization when the plastic flow of rubber reaches a maximum. The greatest possible surface developed during milling is the prerequisite for maximum decrease in surface energy or maximum transformation of work into a bond of filler-rubber, which is stronger than the cohesion of the rubber molecules themselves.

From above considerations it would seem evident that the final reënforcement of a rubber compound is governed and defined by the following three fundamental factors:

(1) The free surface energy of the system, a measure of which is the interface between rubber and pigment in square meters per kilogram of compound. This will be influenced to a considerable extent by the particle size, shape, uniformity, and dispersion of the pigments.

(2) Intensity of wetting of the pigments by the rubber, or of rubber by the pigments. It can be expressed in the numerical difference in dynes per centimeter or ergs per square centimeter between the surface tension of the pigment against air and its interfacial tension against rubber, according to theories developed by Bartell and Osterhof (*1*). This will be regulated by the dispersion, the nature of the rubber and pigment surfaces, and by surface-active substances adsorbed in the interface.

(3) The strength of the rubber matrix in kilograms per square centimeter. This will be influenced by degree of polymerization, state of globular structure, action of dissolved substances and compounding ingredients.

Microscopic Structure of Crude and Masticated Rubber

Experimental results presented by Freundlich and Hauser (*6*), Sebrell, Park, and Martin (*23*), Van Rossem (*27*) and others indicate that ordinary rubber is a very closely packed mass of discrete latex globules. The increase in plasticity upon milling is due to their partial destruction. The milky whiteness characteristic of wet rubber is well known. The lyophilic protein layer between the latex globules absorbs considerable amounts of water, changing the index of refraction of the structural phases.

Samples of rubber were put through the mill to assure uniform thickness of approximately 2.50 mm. Two grams of each sample were then boiled with 100 cc. of water for different lengths of time. Slides were prepared as quickly as possible after extraction, by squeezing the sample between glass slides and sealing the edges with Canada balsam. Microscopical examination of thin sections of rubber that has been thus treated with water gives indications in regard to its structure. Smoked sheets (Figure 1) that had been treated with water for only 4 hours showed a typical granular structure under the microscope, interspersed, however, with clear homogeneous areas optically empty, indicating that the original structure had been destroyed to a certain degree during coagulation and sheeting at the plantation and probably during the treatment with water and preparation of the

slides. Unmilled rubber that had been treated with water for 72 hours absorbed about 3 per cent of water (increase in weight). The water extract of the rubber became more and more acid with prolonged extraction, showing a pH of 5.2 (colorimetrically) after 48 hours and 4.5 after 144 hours, indicating a decomposition of the natural resin glycerides and liberation of organic acid.

Blended sheets that had been broken down for from 2 to 90 minutes showed a gradual destruction of the granular structure. The small rubber globules seemed capable of more resistance toward disintegration than the larger ones (Figure 2). Dead milled rubber did not give the opaque color, the granules had disappeared to a great extent, and the proteins now appeared in the rubber mass in form of large aggregates. The natural rubber resins also aggregated more and more during the milling operations. Rubber that had been extracted with acetone when treated with water showed the granular structure to have disappeared completely.

These microscopical results verify certain observations previously made by Klein and Stamberger (*18*). These authors, however, worked with benzene solutions of rubber and not with the crude rubber itself, as in this investigation.

Crude rubber when mixed with sulfur and treated with water showed that introduction of sulfur into rubber also had brought about a destruction of the granular structure. Similar experiments made with compounds containing zinc oxide and carbon black proved negative, as the minute particle size of these pigments, which is considerably less than the diameter of the latex globules (0.1 to 0.5 micron as compared to an average of 2 microns for latex according to Hauser) hides the appearance of the globules and makes it impossible to conclude whether they still persist or are destroyed. Considering the decrease in plasticity encountered in case of zinc oxide (*17*), it may be possible that the granules are destroyed to a greater or less degree.

Carbon Black

Particle Size and Shape—The question of particle size and shape of carbon black is of considerable importance and very little experimental work on this subject has so far appeared in the literature. Investigations by Spear and Moore (*24*), Peterfi (*20*), and more recently Goodwin and Park (*8*, *a* and *b*), and Hock (*15*) show the difficulty in obtaining a complete dispersion of the black. The particle size of the pigment as dispersed in rubber is not necessarily the same as individual or primary particle size. In a previous paper (*10*) it has been shown that it is possible to distinguish between different types of black from the degree of pigmentation of a mixture of rubber and carbon black, containing 0.5 per cent of pigment. This method, however, gives an indication of the dispersability of the black but not of the ultimate particle.

size. The particle-size determination is extremely difficult, especially in case of different types of gas black.

In order to study the individual particle size, several 0.1-gram samples of gas black have been dispersed in a mixture of ether-alcohol (50:50) with 0.01 per cent of saponin as protective colloid and allowed to stand for 12 hours to obtain sedimentation of undispersed and aggregated material. The clear supernatant fluid was then examined ultra-microscopically. It was found that the suspensions apparently contained individual, practically spherical particles which were estimated to range in an order of magnitude from about 15 to 200 mμ.

The actual shape of the particles was studied, using an Aximuth stob (*26*). It was found that the suspensions contained both isotropic and anisotropic particles, the anisotropic having a much greater tendency to aggregation than the isotropic. The observation evidently conforms with unpublished work of H. Mueller, who by theoretical reasoning assumes a difference in the rate of coagulation between spherical and non-spherical particles. This perhaps explains variations in dispersability of different batches of the same black frequently encountered in rubber compounding.

X-Ray Examination—Debye and Scherrer (*3*) have derived an equation connecting breadth of diffraction lines of crystalline particles with particle diameter. X-ray experiments were performed to establish if this also holds true for carbon black. Previous work reported by Pickles (*21*) and Goodwin and Park (*8a*) mentions the same type of patterns with a breadth of line which follows the microscopically estimated order of particle size.

X-ray photographs were taken of various types of black, the particle size of which was determined microscopically, the blacks being dispersed in rubber in a concentration of 30 per cent. Practically identical patterns were obtained in all cases, probably due to a superimposing of rubber and pigment patterns, and it was not possible to discriminate between the different samples, although the particle size of the various blacks probably ran from an average of 0.1 to 0.4 micron. It also seems that the x-ray method gives indications only in regard to the ultimate unit particle or crystal, but not in regard to its distribution or dispersion. The same patterns were obtained both when the pigments were well and poorly dispersed.

When these blacks were compressed in the form of powder in gelatin capsules for 2 minutes under 50 pounds (3.5 kg. per sq. cm.) pressure and photographs taken the broadening of the diffraction lines mentioned by previous authors was observed with increasing particle size. In cases where the differences in particle size were very small the patterns became more and more alike, and in such cases it is necessary to measure the line breadth of the diffraction spectra photometrically to be able to discriminate between different samples.

The hexagonal symmetry of graphite (*4*, *5*, *16*) and the anisotropic particles observed ultra-microscopically in carbon-black suspensions seem to support claims that the blacks are composed of a mixture of crystalline and amorphous carbon.

WETTING CAPACITY—The wetting capacity of gas black was studied both in water suspension and in rubber. A series of buffer solutions was made up ranging from a pH of 2.2 to 8, using McIlvaine's citric acid–phosphate standards. 0.2 cc. of a 0.001 *M* solution of fuchsin and 50 mg. of gas black were added, and the suspension was incubated at 100° C. Triple-distilled conductivity water of a pH of 7.1 (colorimetrically) was used in this work. It was found that the dye was ab-

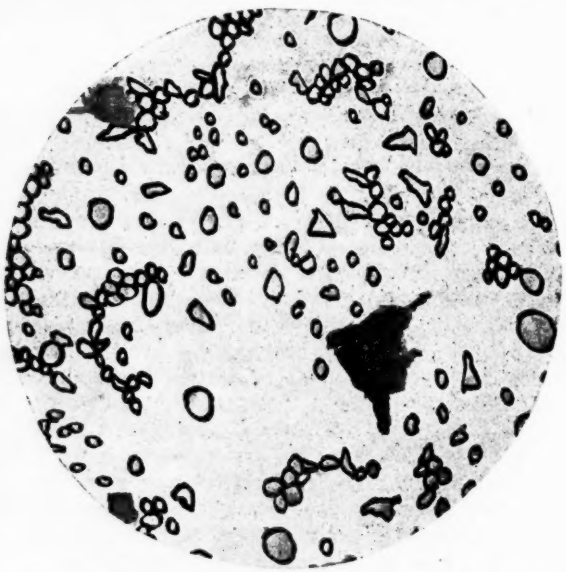

Figure 2—20-Minute Breakdown. Microscopical Drawing Approximately 5000 ×

sorbed readily by the carbon black in buffer solutions on the acid and alkaline sides, but more slowly around the neutral point. The control solutions (buffer and fuchsin) did not show any alteration of the color. The same result was obtained when the pH of the aqueous medium was adjusted by addition of acid or alkali. It was concluded that the adsorption power of carbon black reached a minimum around the neutral point and increased on the acid and alkaline sides, although there was no noticeable difference in the rapidity of absorption at a pH of 6 or that of 2.

It was not possible to establish the presence of any water-soluble chemically active ingredients. When 1 gram of carbon black was digested with 100 cc. of boiling water of pH 7.1 under reflux for 1 hour and then filtered, there was no

change of the pH of the water. The alkali absorption of the black was 1.90 per cent (NaOH and phenolphthalein); the acid absorption none (HCl and phenolphthalein). The acetone extract was 0.18 per cent.

The wetting of carbon black in compounded and cured rubber or the intensity of the bond pigment-rubber was studied. Microscopical sections of highly compounded tread stocks containing about 25 per cent of carbon black were prepared and studied under stretch. Small pieces of cured treads were stretched 200 to 300 per cent and placed in solid carbon dioxide until completely frozen. Small pieces of this stretched, hard, and frozen compound were now cut at right angle against the stretch, and, immediately before any recovery had taken place, immersed in a solution of sulfur chloride in carbon bisulfide. The samples were hardened and sections prepared in the usual way.

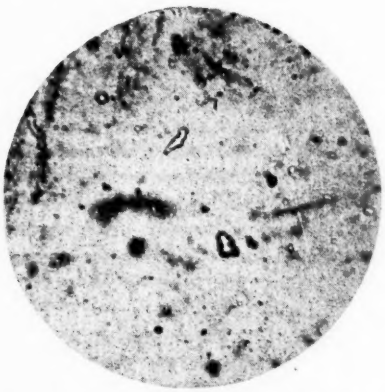

Figure 3—Crude Rubber at 140° C. 600 ×
The distinct white masses are resin aggregates. The black areas represent dust and impurities present in the rubber.

The stretched microsections of cured carbon-black treads showed a marked formation of vacuoles elongated in the direction of stretch, indicating that the bond between pigment and rubber had been broken in various places, but chiefly around aggregates of black or other pigments. (See also Green, *9*.) It was not possible to establish any change in the distribution or orientation of the individual carbon-black particles. This seems to conform with observations by Stamberger (*25*), who has come to the conclusion that with carbon black the adsorption probably involves the formation of a new gel structure, the structure of the original rubber which has been destroyed by milling being in effect restored.

Vulcanization

The dispersion of pigments in rubber during vulcanization as reported in a previous paper has been further studied, but

in this case the whole process has been watched continuously under the microscope. Various compounds were cured in a steam-heated micropress developed by Hauser and Hunemorder (*13*). (See also Hauser, *11*.) The investigations are not yet concluded, but a short summary will be given of the most important results obtained.

CRUDE RUBBER—When unmilled smoked sheet was heated for 16 minutes at 140° C., distinct brownish masses began to appear in the focus of the microscope, indicating a gradual formation of resin aggregates (Figure 3). They showed no signs of melting or decomposition when the rubber was heated to 150° C. or above. The resin glycerides evidently are adsorbed originally in a highly dispersed state on the surface of the latex globules and probably to a great extent remain in such a state when the coagulation process is concluded. The formation of resin aggregates seems to be due to a destruction of the rubber structure by heat in the same manner as during mastication. (Compare with section on microscopic structure. See also Fry and Porritt, 7.) The solubility and chemical reactivity of these aggregated resins are naturally decreased to a great extent when they change from the highly dispersed to the aggregated state. The crude rubber exhibited a pronounced plastic flow during the heating, which ceases very slowly.

RUBBER AND SULFUR—The mobility of the rubber comes to a very sudden stop during the first minutes of heating if sulfur or sulfur and accelerator are added to the system, as has been also brought out by Hauser (*11*). Aggregation of resin crystals takes place when rubber is heated with sulfur, and in addition there seems to be a crystallization of various mineral matter. In this case, however, the resin aggregates show dissolution and disintegration to a certain extent and it seems that a reaction takes place between the rubber resins and the sulfur (*28*).

During milling some of the sulfur particles are dissolved in the hot rubber on the mills and crystallize out in form of small rhombic crystals when the mass cools (Figure 4). These rhombic crystals disappear (Figure 5) during vulcanization at a low temperature, around 60° C., without any noticeable melting, as was established by using an electrically heated "Quetschkammer," where the temperature could be raised gradually from room to vulcanization temperature. They seem to sublime directly into the rubber. This fact is of importance as solution of sulfur in rubber evidently is a prerequisite of vulcanization. The large undissolved particles slowly assume a more and more spherical shape and finally melt at about 120° C., forming large globules. These slowly decrease in size, the speed depending on the accelerator and other compounding ingredients present in the system (Figures 6 and 7). From a dispersion point of view the presence of the small rhombic crystals is advisable. The large sulfur particles when melting usually produce an aggregation of

adherent carbon-black particles as has been shown in a previous paper (*10*). After the heating is discontinued, a crystallization of free sulfur takes place at different lengths of time, depending on the compounding ingredients used. Various types of sulfur crystals are encountered which have been studied and described in detail by Hauser (*11*) and others.

ZINC OXIDE AND CARBON BLACK—The observations in

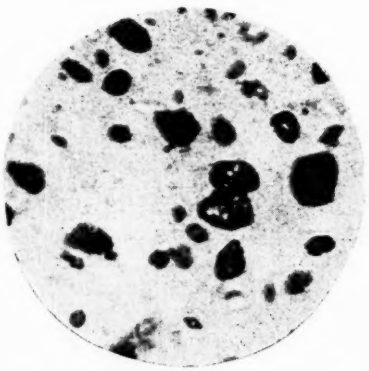

Figure 4—Recrystallized rhombic sulfur crystals and large undissolved sulfur particles at 140° C. at the beginning of vulcanization. The rubber exhibits plastic flow in the direction to the left.

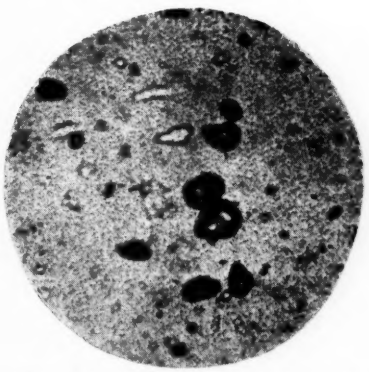

Figure 5—Two minutes at 140° C. The rhombic sulfur crystals have disappeared and the plastic flow of the rubber beginning to cease.

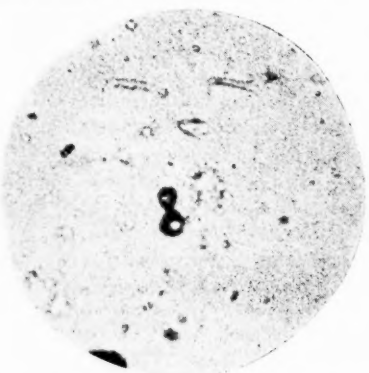

Figure 6—Ten minutes at 140° C. The last traces of sulfur are disappearing.

Figure 7—Forty-five minutes at 140° C. Distinct pigment aggregates are visible.

Figures 4 to 7—Rubber-Sulfur-Carbon Black-Zinc Oxide-Stearic Acid-Di-*o*-tolylguanidine. 600 ×

regard to the dispersion of zinc oxide and carbon black during vulcanization can be summarized as follows: When zinc oxide was added to a rubber-sulfur mixture and the system heated, a dissolution of pigment particles was observed. This evidently was due to the formation of soluble zinc soaps (*19*, *2*). The flocculation of pigments in a mixture containing 5 per cent of zinc oxide was most prominent during the first

minutes of vulcanization (140° C.), but was followed by deflocculation. When rubber was heated with carbon black alone, there was a considerable flocculation of the pigment even though no sulfur was present due to an increased mobility of the rubber. The resin crystals had a great adsorptive tendency towards the carbon-black particles and frequently acted as nuclei for aggregates, as was shown in a previous paper (*10*). The formation of crystals from the free sulfur was considerably inhibited by the carbon-black particles, this probably being partly due to their adsorptive capacity toward sulfur and partly because they fill up the rubber matrix forming a close network, which prevents the formation of large sulfur crystals in the rubber.

STEARIC ACID—When stearic acid was added to the above rubber compounds there seemed to be a greater formation of resin aggregates during mastication than in previous cases, perhaps because the rubber structure was destroyed to a greater extent. The plastic flow of the rubber increased during vulcanization.

ACCELERATOR—The effect of various accelerators as noted under the microscope during vulcanization was characterized by the speed with which the sulfur disappeared from the system. This varied from 3 to 15 minutes, depending on the accelerator and type of compound, when the temperature was raised immediately to 140° C. at the beginning of vulcanization. The plastic flow of the rubber and the length of time until the free sulfur began to crystallize out also varied with different accelerators.

ACETONE-EXTRACTED RUBBER—When extracted rubber was heated under the microscope the plastic flow of the rubber increased tremendously, because the original rubber structure had been destroyed. (Compare with section on microscopic structure.) It was very difficult to disperse the pigments on the mill. The zinc oxide showed a greater tendency to form secondary particles during vulcanization than carbon black. The free sulfur crystallized out almost immediately after the system had cooled down.

Acknowledgment

The author wishes to express his thanks to E. A. Hauser for his advice and suggestions in regard to the experimental work which was, in part, carried out in connection with his course in applied colloid chemistry at Massachusetts Institute of Technology during the summer of 1928. He also acknowledges his indebtedness to E. P. W. Kearsley, of the Fisk Research Laboratories, for help received in the experimental work, and to Messrs. Aborn and Brown, of the x-ray laboratory in the Department of Applied Chemistry at Massachusetts Institute of Technology, for information and kind interest in the study of carbon black.

Literature Cited

(1) Bartell and Osterhof, Colloid Symposium Monograph, Vol. V, p. 113 (1927).
(2) Bedford and Winkelmann, IND. ENG. CHEM., **16**, 32 (1924).
(3) Clark, "Applied X-Rays," p. 179, McGraw-Hill Book Co., New York, 1927.
(4) Debye-Scherrer, *Phys. Z.*, **17**, 277, 283 (1916).
(5) Ewald, *Sitzb. math. physik. bayer.*, Nos. **325–7** (1914).
(6) Freundlich and Hauser, *Kolloid-Z.*, Erg. Bd., **36** (1925).
(7) Fry and Porritt, *Trans. Inst. Rubber Ind.*, **3**, 203 (1927).
(8) Goodwin and Park, IND. ENG. CHEM., **20**, (*a*) 621, (*b*) 706 (1928).
(9) Green, *Ibid.*, **13**, 1029 (1921).
(10) Grenquist, *Ibid.*, **20**, 1073 (1928).
(11) Hauser, Colloid Symposium Monograph, Vol. VI, p. 207 (1928).
(12) Hauser, Gow Lectures, p. 38, London, 1928.
(13) Hauser and Hunemorder, *India Rubber World*, **79**, 59 (1928).
(14) Hock, *Kautschuk*, **1926**, 131; **1927**, 207; *India Rubber J.*, **74**, 419, 453 (1927).
(15) Hock, *Kautschuk*, **1928**, 262.
(16) Hull, *Phys. Rev.*, **20**, 113 (1922).
(17) Hurlston, *Trans. Inst. Rubber Ind.*, **2**, 276 (1926).
(18) Klein and Stamberger, *Kolloid-Z.*, **35**, 362 (1924).
(19) Martin and Davey, *J. Soc. Chem. Ind.*, **44**, 317T (1925).
(20) Peterfi, *Kautschuk*, **1927**, 196.
(21) Pickles, *Trans. Inst. Rubber Ind.*, **2**, 85 (1926).
(22) Pohle, *Z. wiss. Mikroskop.*, **44**, 183 (1927).
(23) Sebrell, Park, and Martin, IND. ENG. CHEM., **17**, 1173 (1925).
(24) Spear and Moore, *Ibid.*, **17**, 936 (1925); **18**, 418 (1926).
(25) Stamberger, *Kolloid-Z.*, **42**, 295 (1927).
(26) Szegvary, *Z. Physik*, **24**, 91 (1923); **25**, 248 (1924).
(27) Van Rossem, *Chem. Weekblad*, **20**, 9 (1923).
(28) Weber, Orig. Com. 8th Intern. Cong. Appl. Chem., **9**, 95.
(29) Wiegand, *India Rubber J.*, **73**, 31 (1927).

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On the Reduction of Rubber Stress-Strain Determinations[1]

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In this paper the authors seek means of eliminating the personal equation in the selection of rubber stress-strain data.

It became necessary to determine the most probable or true values for tensile strength, elongation, and intermediate values. The authors, therefore, tested a complete inner tube, securing ninety-five breaks, which were then reduced by statistical methods.

Frequency distributions of rubber stress-strain data do not strictly obey the law of accidental error, being negatively skewed for breaking values, and positively skewed for intermediate tensiles.

The true values, therefore, are not the arithmetic means but the modes, which are found to differ from the arithmetic means in every case to an extent greatly exceeding the probable error of such means.

Using these true values, and dividing the ninety-five breaks into successive groups of five, the latter were weighted according to four empirical methods and the results compared with the modal values.

The method of selecting three highest elongations out of five together with corresponding tensiles was found most closely to approach modal values. This method is therefore tentatively advanced as a starting point for the standardized selection of rubber breaks.

[1] Presented before the Boston Group Meeting of the Division of Rubber Chemistry of the American Chemical Society, January 12, 1929.

THE excellent report of the Physical Testing Committee (*1*)* illustrates the trend towards increased accuracy in rubber testing; as also the recent investigation of the effect of temperature on physical properties (*2*). The present study is confined to the experimental data themselves, and to the application of statistical methods in their analysis. Determinable (instrumental) errors are excluded from this survey.

In most laboratories it is customary to break three, five, or possibly seven test pieces of a rubber specimen, and to take the arithmetic mean of the resulting values, first rejecting such as appear to the operator to be clearly "wild." In order to work out a scheme for the treatment, or weighting, of such testing data, that shall be free from the vagaries of personal judgment, it is first necessary to determine, with the utmost precision possible, what are the true values of the quantities in question. Since the reliability of the average value of N tests is $\sqrt{N}$ times as accurate as that of one test, an increase in the number of test pieces broken suggests itself as one obvious step in arriving at the desired "true," or more strictly, most probable, values.

Experimental

A factory-run inner tube was cut longitudinally, and the total number of available test pieces cut across the grain—ninety-five—were died out. These pieces were then thoroughly mixed, selected at random, and tested on a Scott machine. The test pieces were of dumbbell shape, $^1/_4$ inch wide, 1 inch between bench marks (machine of standard pattern), speed of separation 20 inches per minute. Intermediate as well as breaking values were secured. (See Table I for breaking data.)

EFFECT OF NUMBER OF TESTS ON ERROR OF ARITHMETIC MEAN—Consider first breaking tensiles as shown in Figure 1. In order to trace the effect of increasing the number of tests on the arithmetic mean, progressive values for such means are shown, each dot on the graph indicating the arithmetic mean of all tests up to that point. Note the irregular trend of the arithmetic mean values, particularly in the early stages. Only after sixty breaks does the mean settle down to its final value as measured by the ninety-five breaks. The probable error of the mean

$$\epsilon_M = \pm 0.67 \sqrt{\frac{\Sigma\rho^2}{n(n-1)}}$$

as indicated in the graph by the heavy bands, has decreased from a value of 36 pounds for five breaks, and 17 pounds for fifteen breaks, to 12 pounds for ninety-five breaks.

Thus it is seen that when ninety-five test pieces are broken in place of the customary five, and the arithmetic means determined in each case, the value for tensile strength

* Italic numbers in parenthesis refer to literature cited at end of article.

of the inner tube would seem to be 2637 pounds with a probable error of ±12 pounds.

There is, however, a fallacy in this conclusion. This arises because the data have been treated on the assumption that they obey the law of accidental error. As shown in Figure 2, this law assumes symmetrical distribution about the true, or most probable, value. For such a distribution the arithmetic mean constitutes the true value, and the greater the number of tests the more reliable and accurate is this form of "average." The data of the experiment, however, do not follow this law.

DETERMINATION OF TRUE (MODAL) BREAKING TENSILE—In Figure 3 are shown the number of occurrences of each tensile value in the ninety-five tests. It will at once be noted that this frequency curve does not follow the law of accidental error. Instead of being symmetrical, the curve is lopsided or "skewed" (*5*, *4*) towards the left or the low values; there is a preponderance of low breaks, due presumably to flaws in the rubber.

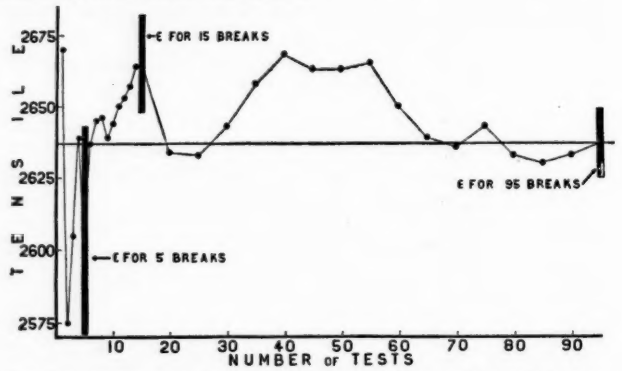

Figure 1—Number of Tests *vs.* Arithmetic Mean and Probable Error of Arithmetic Mean

The curve of Figure 4 is that generated by the histogram of Figure 3. The arithmetic mean is no longer the most frequently occurring and therefore the most probable or true value. This quantity is defined as the "mode" and is seen to show a distinctly higher value (*3*).

In Figure 5 the "true" or modal value for tensile is compared with the values for the arithmetic mean (Figure 1). In no case does the arithmetic mean reach the mode, all the values being lower, and in no case does the probable error of the arithmetic mean overtake this deviation. Increasing the number of test pieces, even up to ninety-five, although reducing the probable error of the arithmetic mean, does not simultaneously reduce its inaccuracy. In fact, after ninety-five tests, the arithmetic mean falls short of the mode by more than five times its own probable error.

DETERMINATION OF TRUE INTERMEDIATE TENSILES—Examination of Figure 6 shows that, as in the case of breaking

Table I—Breaking Data

Sample	Gage of Sample	Tensile at 300% Elong.	Tensile at 500% Elong.	Tensile at Break	Elongation at Break
	Inch	*Lbs./sq. in.*	*Lbs./sq. in.*	*Lbs./sq. in.*	*Per cent*
1	0.069	200	550	2670	770
2	0.067	240	535	2480	740
3	0.072	195	470	2665	790
4	0.068	205	530	2740	780
5	0.074	215	485	2480	770
6	0.069	200	520	2785	780
7	0.069	200	490	2695	780
8	0.067	210	570	2755	770
9	0.070	200	515	2480	760
10	0.067	240	535	2685	770
11	0.068	205	530	2715	770
12	0.067	210	535	2685	770
13	0.068	205	530	2715	770
14	0.070	230	515	2745	780
15	0.072	220	555	2685	780
16	0.068	235	590	2915	780
17	0.071	225	535	2670	770
18	0.072	220	500	2290	750
19	0.073	220	520	2430	750
20	0.073	220	550	2400	750
21	0.073	220	520	2460	760
22	0.075	215	530	2685	780
23	0.074	215	510	2695	780
24	0.070	230	540	2575	760
25	0.073	220	520	2735	780
26	0.072	220	525	2740	780
27	0.071	225	505	2815	780
28	0.076	210	525	2525	770
29	0.068	205	530	2910	780
30	0.070	200	515	2480	760
31	0.069	230	520	2925	790
32	0.070	200	515	2745	780
33	0.071	195	535	2750	780
34	0.072	195	500	2635	780
35	0.069	200	520	2675	770
36	0.069	230	520	2615	770
37	0.069	230	550	2895	780
38	0.072	220	555	2720	760
39	0.070	200	515	2630	770
40	0.070	230	540	2825	780
41	0.071	195	505	2815	790
42	0.073	190	465	2600	790
43	0.070	200	515	2600	770
44	0.068	205	550	2600	770
45	0.071	195	505	2500	770
46	0.072	195	500	2665	780
47	0.071	225	505	2560	770
48	0.068	205	530	2915	780
49	0.069	200	490	2695	780
50	0.070	200	515	2485	750
51	0.069	200	520	2585	760
52	0.070	200	515	2750	770
53	0.068	205	530	2800	780
54	0.069	205	520	2755	770
55	0.068	205	530	2520	750
56	0.074	215	540	2675	770
57	0.081	220	545	2345	750
58	0.074	215	540	2455	750
59	0.073	220	550	2600	760
60	0.069	200	490	2375	760
61	0.070	200	515	2660	770
62	0.085	210	495	2300	750
63	0.078	205	485	2425	770
64	0.083	220	505	2650	770
65	0.071	225	505	2480	760
66	0.082	195	510	2610	770
67	0.074	190	510	2455	760
68	0.071	195	505	2515	770

Table I—Breaking Data (*Continued*)

Sample	Gage of Sample	Tensile at 300% Elong.	Tensile at 500% Elong.	Tensile at Break	Elongation at Break
	Inch	*Lbs./sq. in.*	*Lbs./sq. in.*	*Lbs./sq. in.*	*Per cent*
69	0.073	190	490	2635	780
70	0.069	205	490	2755	770
71	0.071	195	505	2755	780
72	0.069	230	520	2870	780
73	0.067	210	540	2755	780
74	0.070	200	515	2660	760
75	0.070	200	515	2685	780
76	0.069	200	490	1880	720
77	0.068	205	530	2745	780
78	0.068	205	530	2515	750
79	0.072	195	500	2525	760
80	0.068	205	530	2720	760
81	0.070	200	485	2520	760
82	0.067	240	570	2780	760
83	0.068	205	590	2570	750
84	0.072	220	585	2220	720
85	0.067	240	630	2840	770
86	0.074	215	540	2800	770
87	0.065	245	615	2530	740
88	0.066	240	605	2910	770
89	0.070	200	540	2745	760
90	0.071	225	565	2420	740
91	0.065	245	650	2865	750
92	0.066	245	580	2825	770
93	0.069	205	580	2550	750
94	0.073	220	550	2700	770
95	0.070	230	515	2630	760

tensile, the frequency curve is asymmetrical, thus again precluding the use of the arithmetic mean. The "skewness" is here towards the right, or positive, this being clearly due to personal equation in the form of lag in the recording of loads. The "skewness" at 500 per cent is less than at 300 per cent because the bench marks are here separating more slowly. Because the "skewness" is positive, the

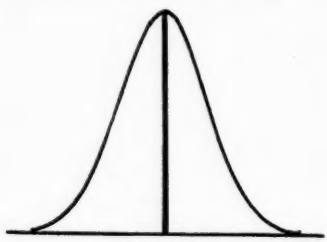

Figure 2—Normal Frequency Distribution

$y = k_e^{-h^2x^2}$

arithmetic means are now higher than the true or modal values, and to a degree again exceeding their own probable errors.

Determination of True Breaking Elongation—Figure 7 shows that the curve is here once more "skewed" towards the left, presumably because of flaws in the test pieces. This "skewness," however, is much less evident

than in the case of tensile, partly because the bench marks are separating very slowly, thus permitting more accurate observation, but chiefly because the stress is increasing much more rapidly than the elongation, and any shortening of the curve due to defects in the rubber has consequently less influence on the elongation than on the tensile. As with breaking tensiles, the arithmetic mean is lower than the mode, the

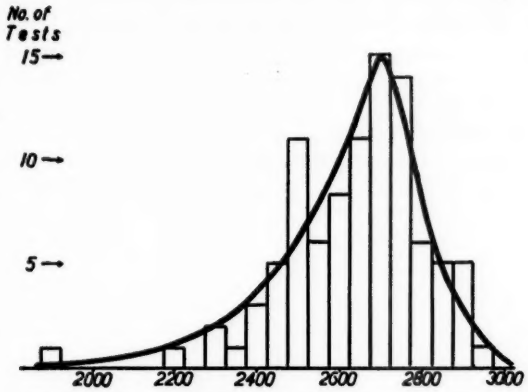

Figure 3—Frequency Distribution, Tensile at Break

difference, although small in absolute terms, being still many times the probable error (of the arithmetic mean).

Reliability of Various Determinations

Figure 8 shows in comparative form the frequency distribution for four critical stress-strain values. Visual inspection will indicate that the degree of concentration around the most probable or modal value is, roughly speaking, similar for all the tensile values, but that the concentration for elongation at break is markedly greater. In other words, the number of "wild" results is much less for elongation than for tensile at rupture or modulus values. (This statement of course applies entirely to bar test-piece technic and not to ring testing.)

Table II—Statistical Summary

Quantity Measured Tensile at:	Arithmetic Mean (95)	Standard Deviation	Coeff. of Variation	Skewness[a]	Mean	Median	Mode
100% elong.	85	3.9	4.63				
200% elong.	136	12.5	9.23				
300% elong.	212	14.6	6.92	+0.58	212	210	204
400% elong.	326	17.4	5.35				
500% elong.	528	32.3	6.11	+0.084	528	528	525
600% elong.	1014	65.1	6.42				
700% elong.	1854	112.4	6.07				
Break	2637	169.6	6.44	−0.39	2637	2670	2703
Elong. at break	767	17.4	2.26	−0.24	767	770	771

[a] Skewness = $\frac{\text{mean} - \text{mode}}{\text{standard deviation}}$.

The exact measure of the reliability is known as the "coefficient of variation" (*6*).

$$v = \frac{\sigma}{M} \times 100 \text{ per cent}$$

where v = coefficient of variation, σ = standard deviation from mean, and M = mean

It is seen from the coefficients of variation given in Table I that the reliability of the elongation at break is approximately three times as great as that of the other values.

Application to Laboratory Test Procedure

The discussion thus far has been confined to the influence of increasing the number of breaks upon the accuracy of the final result. This has brought out the necessity for recognizing and evaluating the "skewed" nature of rubber

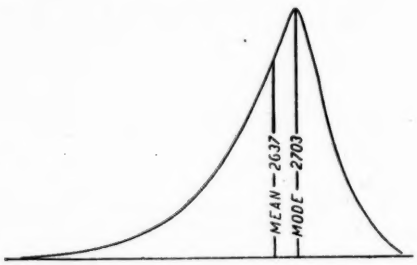

Figure 4—Frequency Distribution, Tensile at Break

stress-strain tests. It is, of course, impracticable in the course of daily control, and even of research testing, to carry out sufficient breaks or intermediate readings to generate and evaluate a frequency curve in each case. To do this would require upwards of sixty tests. The problem is one of weighting a small number, say five tests, so as to approximate the truth.

It is common practice in laboratories to reject what are loosely defined as "obviously wild" results, but there is a disagreement as to what constitutes a "wild" result. A rule favored by some is that only such values shall be rejected as show a deviation four times greater than the average deviation of the remainder. This rule fails to eliminate admittedly "wild" results. More specifically, of the ninety-five tests described in the present study, this rule would have eliminated only one, thus leaving the "skewness" of the frequency curves substantially uncorrected. A determination of the modal value would therefore still be necessary. Some other means of weighting is clearly required in order that "mean" values may yield more nearly true results. Several empirical methods of weighting have therefore been applied.

The ninety-five tests on the inner tube mentioned above have been divided into nineteen successive groups of five, thus, in effect, constituting nineteen "laboratories" working under exactly comparable conditions and on the same material. (See Tables I and III.) It was thought that this procedure was the only way in which irrelevant variables could be eliminated so that final results should be amenable to statistical treatment.

Treatment has been confined to tensile strength and elongation at break, these being the most popular tests, and also because the intermediate values are free from negative "skewness" due to flaws, and consequently greater symmetry of distribution is to be obtained, not by weighting, but by refinement of technic—e. g., reduction in the personal lag. As a means of evaluating the various weighting schemes, the corresponding tensiles obtained from the

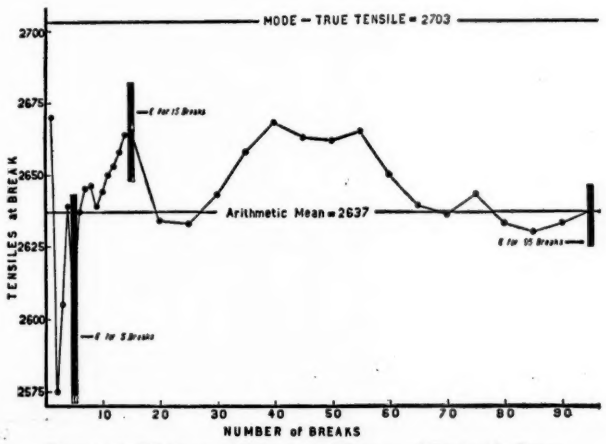

Figure 5—Mode *vs.* Arithmetic Mean and Probable Error

nineteen "laboratories" were averaged, and deviations of the "laboratories" from the true or modal value noted.

Method 1—Mean of All Five Tensiles, Equal Weights. The average for the nineteen "laboratories" is, of course, 2637 pounds—the arithmetic mean of the ninety-five tests—and as such lies well below the mode (2703). Of the nineteen "laboratories," six were more than 100 pounds off the modal value, two being off by more than 200. The elongation by this method is 767 per cent against a mode of 771 per cent.

Method 2—Mean of Best Two Tensiles. The average for the nineteen "laboratories" here gives a value of 2769 which is well above the modal value. In this case eight "laboratories" were off more than 100 pounds, the elongation by this method being 775 per cent.

Method 3—Mean of Tensiles Corresponding to Best Two Elongations. The average for the nineteen "laboratories" gave 2757 pounds; still high: seven "laboratories" off more than 100 pounds; elongation 776 per cent.

Method 4—Mean of Tensiles Corresponding to Best Three Elongations. The average for the nineteen "laboratories" was 2717 pounds as compared to the mode of 2703, a difference of only 14 pounds. In this case only five "laboratories" were off more than 100. Elongation by this method stands at 772 per cent against a mode of 771 per cent.

Inspection of Table IV clearly brings out the superiority of Method 4.

It is necessary to emphasize that the above weightings are purely empirical. It is also necessary to emphasize that the scheme of weighting found best for the data of the present paper might not be applicable to another set of tests using different equipment and employing compounds of different type.

With these limitations in mind, it is suggested that the selection of the three highest elongations out of five breaks,

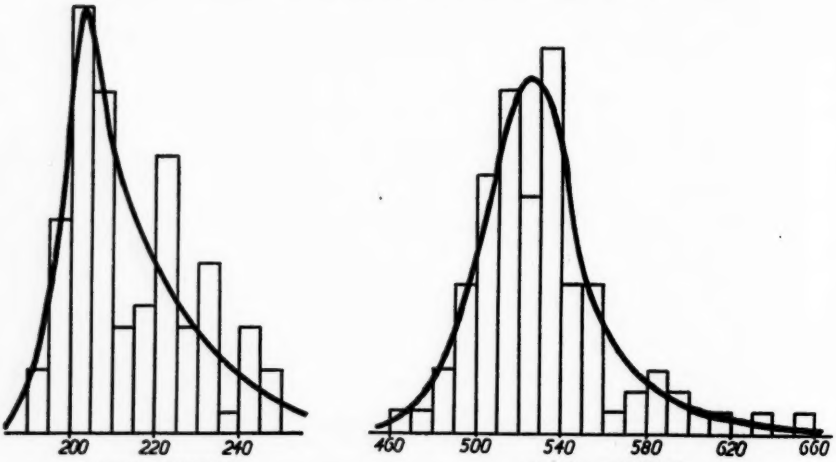

Figure 6—Frequency Distribution at Intermediate Elongations

together with the corresponding tensiles, be given consideration in the development of some standard method of weighting rubber stress-strain data. Irrespective of the question of approximation to modal or true values, the scheme of the three best elongations has the important practical advantage, at least with the ordinary bar test-piece machine, that the operator can give effect to his rejections immediately the breaks are finished and without first working out all of the tensile strengths—in fact, without any preliminary arithmetic.

It is suggested that other rubber laboratories take enough time to select, say two or three "type" compounds, and vulcanize samples of sufficient size to supply upwards of sixty test pieces; that these be broken under strictly comparable conditions of temperature, humidity, etc.; that the frequency curves be plotted for intermediate tensiles, tensile at

Table III—Comparison of Methods of Weighting

Laboratory	Method 1 Tensile	Method 2 Tensile	Method 3 Tensile	Method 3 Elong.	Method 4 Tensile	Method 4 Elong.
	Lbs./sq. in.	*Lbs./sq. in.*	*Lbs./sq. in.*	*Per cent*	*Lbs./sq. in.*	*Per cent*
1	2607	2705	2705	775	2692	780
2	2680	2770	2740	780	2745	777
3	2709	2730	2715	780	2715	777
4	2541	2792	2793	775	2672	760
5	2630	2715	2710	780	2705	780
6	2694	2863	2863	780	2822	780
7	2746	2838	2835	785	2807	783
8	2737	2860	2860	780	2783	777
9	2623	2708	2708	790	2672	783
10	2664	2805	2805	780	2758	780
11	2682	2776	2778	775	2768	773
12	2490	2638	2638	765	2550	763
13	2503	2655	2655	770	2578	770
14	2594	2695	2695	775	2666	777
15	2745	2813	2818	780	2793	780
16	2477	2733	2635	770	2663	767
17	2586	2810	2810	765	2713	733
18	2681	2855	2855	770	2818	767
19	2714	2845	2763	770	2718	767

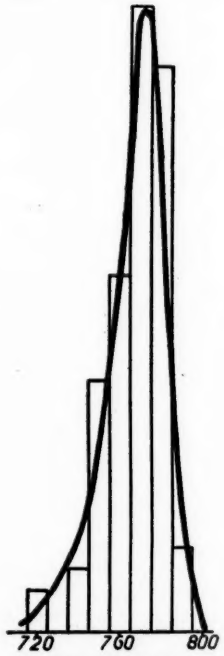

Figure 7—Frequency Distribution, Elongation at Break

break, and elongation at break; that modal values be ascertained; and then that the tests be split up in some such manner as has been here outlined, and a scheme of weighting evolved which shall, for the type compounds in question and for the specific laboratory, yield the closest approximation to the truth. It is possible, and even probable, that no two laboratories and that no two compounds will yield the desired results from the same scheme of weighting.

Table IV—Variation from Mode (Tensile at Break) by Different Weighting Methods

Relation to Mode	Number of Laboratories			
	Method 1	Method 2	Method 3	Method
Above	5	16	15	13
Below	14	3	2	6
±50 pounds or more	9	12	12	9
±100 pounds or more	6	8	7	5
±150 pounds or more	4	3	3	2
±200 pounds or more	2	0	0	0

On the other hand, there is a possibility that the scheme of the three best elongations out of five, here described, or some variation of this scheme, will be close enough to the truth to provide the basis for a standardized treatment, the urgent need for which is self-evident.

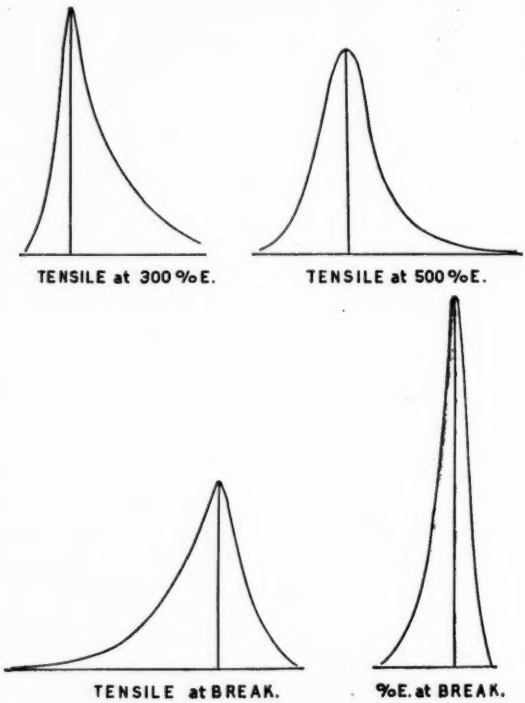

Figure 8—Comparison of Frequency Distributions

Addendum

Since writing the above paper, the authors have noticed a study, "Essais mécaniques du caoutchouc et probabilités," in *Chimie et industrie*, April, 1928, by M. R. Fric. It is a pleasure to acknowledge this prior publication of experiments carried out upon "pure" rubber specimens using Schopper rings, in the course of which the author established the approximate validity of the law of accidental error as applied to 731 breaks.

Those interested in the theory of probabilities will find in Fric's paper an elegant alternative treatment of the breaking tensile data in the form of Ogive curves. By means of these, he clearly demonstrates the abnormal frequency of low values which he ascribes to flaws in the rubber. It is thus seen that

the preliminary part of the present paper stands as an independent confirmation of Fric's observations. The present authors were, of course, primarily interested less in the ultimate reduction to most probable values than in the development of methods for weighting a small number of tests.

Literature Cited

(1) Physical Testing Committee, A. C. S. Division of Rubber Chemistry, IND. ENG. CHEM., **20**, 1245 (1928).
(2) Somerville and Cope, *India Rubber World*, **79**, No. 2, 64 (1928).
(3) Sutcliff, "Elementary Statistical Methods," pp. 157 and 158, McGraw-Hill Book Co.
(4) Sutcliff, *Ibid.*, Chap. XVI.
(5) Yule, "Introduction to Theory of Statistics," Chap. VIII, C. Griffin & Co.
(6) Yule, *Ibid.*, p. 149.

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Importance of Temperature and Humidity Control in Rubber Testing

II—Resistance to Abrasion[1]

REPORT OF THE PHYSICAL TESTING COMMITTEE OF DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

IN A previous report of the Physical Testing Committee, IND. ENG. CHEM., **20**, 1245 (1928), attention was called to the fact that the temperature of testing has a considerable effect upon the stress-strain relation of rubber compounds and that relative humidity, between the mixing and the curing of the compounds, also affects the stress-strain relation. The committee, therefore, decided to extend the investigation to include the effect of these same variables upon the resistance to abrasion.

Since there is no accepted satisfactory method of determining the resistance to abrasion, it was decided to use two machines which differ quite widely in principle. The machines used in this investigation are the Grasselli abrader, which works upon the Prony brake principle [Williams, IND. ENG. CHEM., **19**, 674 (1927)] and gives results in volume loss per horsepower-hour, and the U. S. abrader, which measures the volume loss per hour. These machines were chosen by the committee, not with the belief that the results obtained by their use were a true criterion of the actual wearing qualities of the compounds under service conditions, but to show the differences in results, if any, due to variations in temperature and humidity during the preparation and testing of samples. The four compounds used are numbers 1, 4, and 5, which were used in the investigation of the stress-strain relation, and another compound designated as number 6. This selection provides for study a laboratory test compound, two high-grade tread compounds containing two widely different types of organic accelerators, and a compound which represents a commercial heel compound. Three cures of each compound were tested. The formulas are given in Table I.

[1] Publication approved by the director of the Bureau of Standards of the U. S. Department of Commerce.

Table I—Test Formulas

Ingredient	Stock 1	Stock 4	Stock 5	Stock 6
Smoked sheets	100	100	100	100
Zinc oxide	5	5	5	12.31
Sulfur	3	3.5	3.5	8.62
Carbon black	..	40	40	43.08
Di-*o*-tolylguanidine	0.75	1.25	..	1.54
Mercaptobenzothiazole	..	..	1.0	..
Stearic acid	..	..	3.0	..
Mineral rubber	..	5.0	..	..
Pine tar	..	2.0	2.0	..
Whole-tire reclaim	..	..	..	278.16
Barytes	..	..	..	123.08
Dixie clay	..	..	..	45.54
Paraffin	..	..	..	3.08

The investigation naturally divides itself into three phases which are:

(1) The study of the four compounds prepared under identical conditions as regards conditioning both in the raw and cured state at 45 per cent relative humidity and 82° F. (27.8° C.) but tested at 15°, 25°, and 35° C.

(2) The study of the compounds conditioned before vulcanization at 10, 40, 70, and 100 per cent relative humidity at 82° F. (27.8° C.) and conditioned cured at 45 per cent relative humidity at 82° F. (27.8° C.) before finally testing at 82° F. (27.8° C.).

(3) The study of the effect of three temperatures 59° F. (15° C.), 82° F. (27.8° C.), and 95° F. (35° C.) while maintaining a relative humidity of 45 per cent during the conditioning of the cured stock previous to testing at 82° F. (28.7° C.).

To control the temperature during testing, the Grasselli abrader was placed in a wooden cabinet and the temperature of the air blast controlled by passing the air through a 100-foot (30.5-meter) coil of $^3/_8$-inch (9-mm.) copper tubing within a bath which was heated or cooled as required. The temperature of the bath was found not to be so important in determining the temperature of the blast when it reached the abrasive as the temperature of the cabinet itself, although necessarily it had some influence. The air of the blast was cooled by expansion, but it also aspirated air of the chamber and mixed with it so that there was no simple relation between the temperature of the blast as it reached the abrasive and the temperature of the bath. Heat was also lost or gained (depending upon the temperature used) between the bath and the orifices in spite of careful lagging of the pipes. Adjustment of temperatures was made by repeated trials and temperatures taken with a thermometer where the blast met the abrasive. Temperatures were taken also by placing a thermocouple in a hole bored in the arm of the machine back of the sample being abraded. This temperature toward the end of a run was from 1 to 2 degrees higher than the temperatures of the blast or cabinet, which were equal. When the samples were being abraded at 15° C., it was found necessary to place a cake of ice in the cabinet and allow an electric fan to play upon it as an auxiliary cooling device to offset the heat generated by the motor.

This method of temperature control was rather crude, but as it was considered impractical to introduce a large amount

of rubber dust into the constant-temperature room of the bureau, the cabinet plan was used. By careful control of temperature of the air blast and constant manipulation of the fan, temperatures were maintained in the cabinet within ±1° C.

When testing with the U. S. abrader, air of a definite temperature controlled within ±1° C. was introduced into the cabinet and well mixed by an electric fan. Ice had to be used at the low temperature, as with the Grasselli machine, to compensate for the heat generated by the two motors of this abrader. Temperatures of the test pieces were taken near the end of the run by placing a thermocouple between the piece and the upper edge of the slot. This temperature was from 1 to 1.5 degrees higher than the temperature of the cabinet.

In testing with the U. S. abrader, the corresponding cures of the four stocks were tested simultaneously and the check run was made by varying the order of the stocks in the different positions. In positions 1, 2, 3, and 4 were placed stocks 6, 1, 5, and 4, respectively, while the duplicate determination was made with positions 1, 2, 3, and 4 occupied, respectively, by stocks 4, 6, 1, and 5. No consistent relationship was found due to changing the position of the stocks in this manner.

In the absence of definite information as to the agreement to be expected between duplicate determinations, it was estimated that the limit of allowable error might be placed at 5 per cent. Hence results were redetermined if the divergence between duplicate runs was greater than 5 per cent. As a result of this ruling only three redeterminations were required during the investigation. In the majority of cases the divergence was about 2 per cent. Each machine showed nearly the same differences between check determinations.

The Grasselli abrader, in general, shows greater differences due to cure than does the U. S. abrader, perhaps because the latter machine requires much larger samples than the Grasselli machine.

No comparison of the relative merits of the two abraders can be made because no knowledge is at hand concerning wear of the compounds under service conditions. Since it is possible to abrade five samples simultaneously with the U. S. abrader, more comparisons can be made with it in the same length of time than with the Grasselli abrader. The ratio in favor of the U. S. abrader in this respect is nearly 2 to 1.

The rubber used in this investigation was taken from the same lot of smoked sheets previously prepared by the Fisk Rubber Company and used in the study of the stress-strain relation.

Part I—Effect of Temperature during Testing

The batches were prepared on a 24-inch (60.9-cm.) mill and, after mixing, the speed of the rolls was reduced so that a uniform sheet 0.10 inch (2.5 mm.) in thickness was obtained. The sheet was then cut into slabs 6 by 6 inches (15.2 by 15.2 cm.) for conditioning at 45 per cent relative humidity at 82° F. (27.8° C.) for 24 hours before curing. In addition, slabs for the middle cure of each stock were conditioned 48 hours and 72 hours before curing. After conditioning, the slabs were removed

from the chambers and plied to proper thickness for the molds. Cured slabs 12 by 2 by $^1/_2$ inch (30.5 × 5.1 × 1.3 cm.) were prepared for the U. S. abrader and the regular molds supplied with the Grasselli abrader were used for the preparation of its test pieces. The slabs for the U. S. abrader were cured in an aluminum frame between thin sheets of aluminum. In all cases the compound was so placed in the mold that abrasion would take place in the direction of the grain.

Table II gives the values obtained with both abraders at the three temperatures. Table III gives results obtained with the Grasselli abrader, disregarding the power consumption. The results of the 24-hour exposures are likewise shown graphically in Charts 1 to 3, inclusive.

From a study of the results, it is evident that within the range of temperature investigated the effect due to temperature during testing varies both in degree and direction with the compound used. These differences amount to as much as 25 per cent with some of the compounds. The results from conditioning the raw stock for longer than 24 hours showed differences only within the range of experimental error, so that no conclusive significance can be attached to them.

Part II—Effect of Relative Humidity between Mixing and Vulcanization

Immediately after mixing and sheeting to a thickness of 0.1 inch (2.5 mm.), the raw stocks were exposed in cabinets to atmospheres of 10, 40, 70, and 100 per cent relative humidities at 82° F. (27.8° C.) for a period of 24 hours before vulcanization. Each compound was given three cures as was done in Part I. In addition, raw stock was exposed for 48 and 72 hours before giving it the middle cure.

Table II—Resistance to Abrasion at Different Temperatures of Testing

(U. S. abrader, expressed in cubic centimeters loss per hour; Grasselli abrader, expressed in cubic centimeters loss per horsepower-hour)

Stock	Time Conditioned before Curing	Cure	Tested on U. S. Abrader at:			Tested on Grasselli Abrader at:		
			15° C.	25° C.	35° C.	15° C.	25° C.	35° C.
	Hours	*Min.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
		At 141.8° C.						
1	24	30	6.47	5.84	4.60	416	360	313
	24	45	5.05	4.72	3.87	290	260	202
	48	45	4.68	4.66	3.80	287	269	206
	72	45	4.72	4.69	3.69	295	269	207
	24	60	4.42	4.18	3.92	252	221	182
4	24	30	4.68	4.69	4.12	316	289	262
	24	45	4.37	4.20	4.25	288	266	244
	48	45	4.31	4.23	4.19	295	269	249
	72	45	4.30	4.01	4.41	293	273	244
	24	60	4.42	3.85	3.96	282	257	240
		At 126.1° C.						
5	24	45	3.11	3.73	3.32	160	220	230
	24	60	3.22	3.05	2.90	194	218	203
	48	60	3.09	3.09	2.79	194	217	197
	72	60	3.13	2.93	2.69	194	218	198
	24	90	2.67	2.55	2.29	184	170	153
		At 157.2° C.						
6	24	9	7.68	9.06	10.47	765	823	903
	24	12	7.99	8.75	11.00	728	766	865
	48	12	7.75	8.71	11.00	719	777	869
	72	12	7.89	8.77	10.99	721	785	872
	24	15	8.02	8.88	10.95	704	755	850

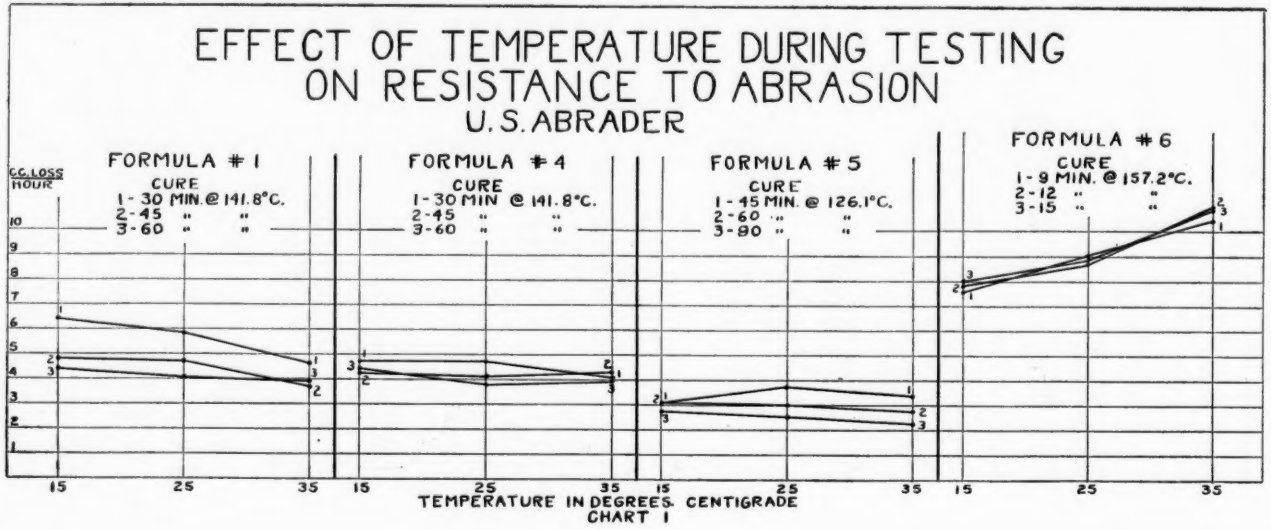
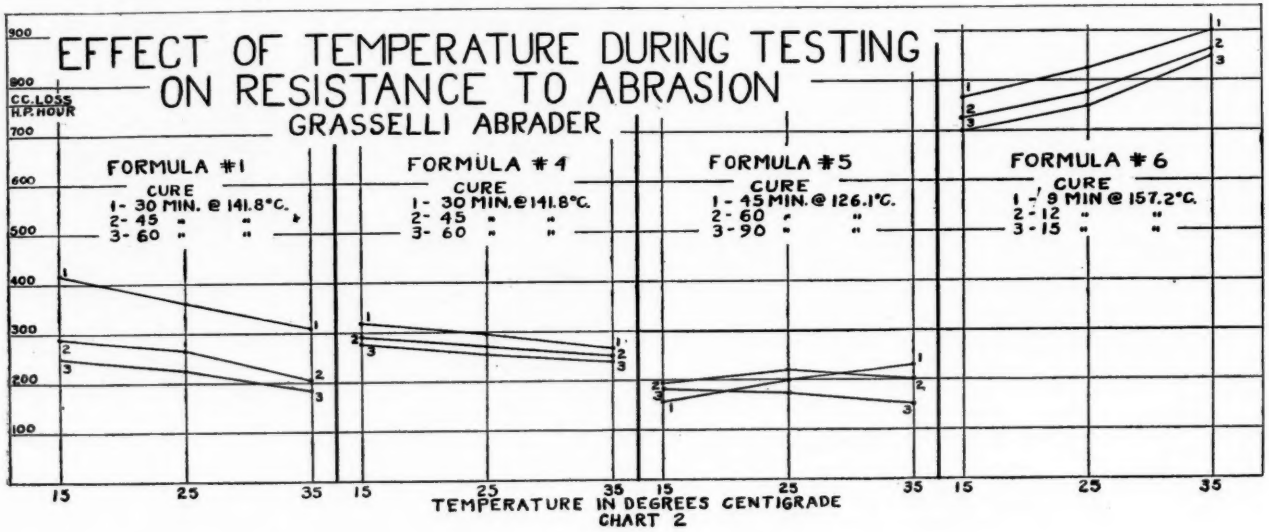

EFFECT OF TEMPERATURE DURING TESTING
ON RESISTANCE TO ABRASION
U.S. ABRADER
FORMULA # 1
CURE
1 - 30 MIN. @ 141.8°C.
2 - 45 " "
3 - 60 " "
FORMULA # 4
CURE
1 - 30 MIN @ 141.8°C.
2 - 45 " "
3 - 60 " "
FORMULA # 5
CURE
1 - 45 MIN. @ 126.1°C.
2 - 60 " "
3 - 90 " "
FORMULA # 6
CURE
1 - 9 MIN. @ 157.2°C.
2 - 12 " "
3 - 15 " "
CC. LOSS / HOUR
10
9
8
7
6
5
4
3
2
1
15
25
35
TEMPERATURE IN DEGREES CENTIGRADE

CHART 1


EFFECT OF TEMPERATURE DURING TESTING
ON RESISTANCE TO ABRASION
GRASSELLI ABRADER
CC. LOSS H.P. HOUR
900
800
700
600
500
400
300
200
100
FORMULA #1
CURE
1- 30 MIN. @ 141.8°C.
2- 45 " "
3- 60 " "
FORMULA #4
CURE
1- 30 MIN. @ 141.8°C.
2- 45 " "
3- 60 " "
FORMULA #5
CURE
1- 45 MIN. @ 126.1°C.
2- 60 " "
3- 90 " "
FORMULA #6
CURE
1- 9 MIN @ 157.2°C.
2- 12 " "
3- 15 " "
15
25
35
TEMPERATURE IN DEGREES CENTIGRADE
CHART 2

EFFECT OF TEMPERATURE DURING TESTING ON RESISTANCE TO ABRASION

GRASSELLI ABRADER

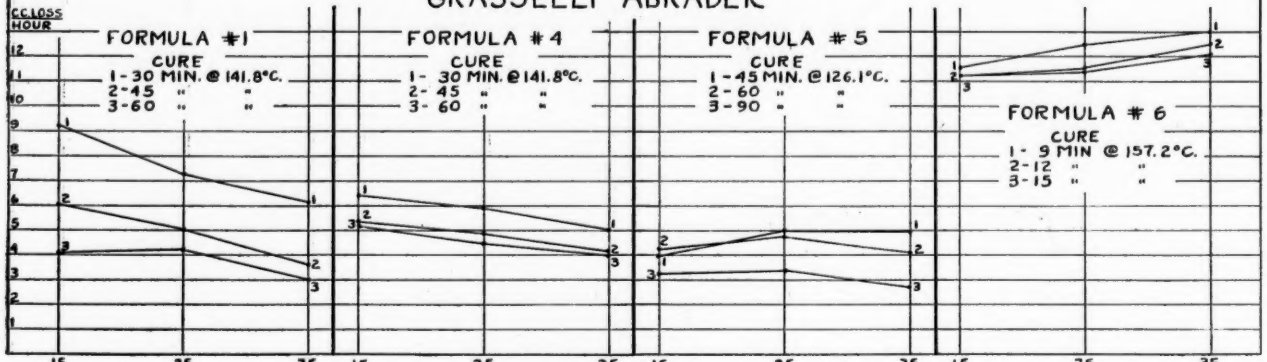


CHART 3

Table III—Resistance to Abrasion at Different Temperatures of Testing on Grasselli Abrader, Disregarding Power Consumption

(Expressed in cubic centimeters loss per hour)

Stock	Time Conditioned before Curing	Cure	Tested at:		
			15° C.	25° C.	35° C.
	Hours	*Min.*	*Cc.*	*Cc.*	*Cc.*
		At 141.8° C.			
1	24	30	9.20	7.25	6.27
	24	45	6.08	5.05	3.61
	48	45	5.98	5.25	3.74
	72	45	6.20	5.20	3.91
	24	60	4.16	4.23	3.01
4	24	30	6.45	5.88	5.02
	24	45	5.27	4.80	4.16
	48	45	5.41	4.87	4.25
	72	45	5.37	4.85	4.18
	24	60	5.20	4.59	4.01
		At 126.1° C.			
5	24	45	3.91	4.91	4.92
	24	60	4.27	4.79	4.10
	48	60	4.27	4.53	3.78
	72	60	4.28	4.71	3.77
	24	90	3.27	3.36	2.74
		At 157.2° C.			
6	24	9	11.57	12.49	12.97
	24	12	11.22	11.58	12.54
	48	12	11.07	11.63	12.48
	72	12	11.12	11.74	12.38
	24	15	11.19	11.41	12.13

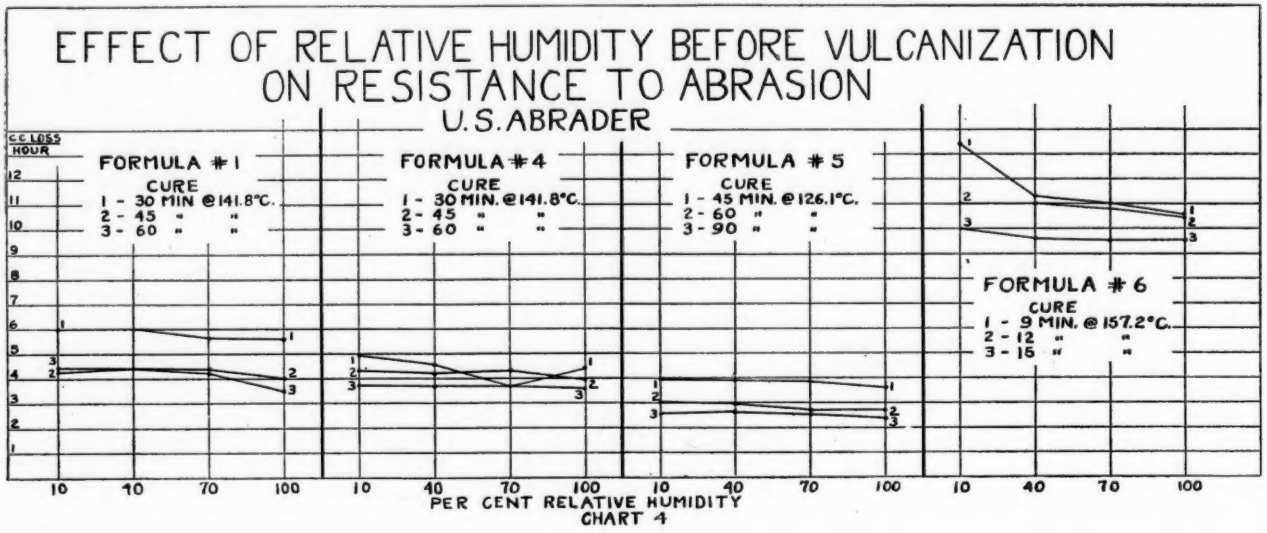
The cured samples were stored in the dark with paper between each sample for approximately a month before the tests were started. This was the procedure previously used in the stress-strain investigation. Before testing the resistance to abrasion at 82° F. (27.8° C.), the samples were given a 24-hour exposure to 45 per cent relative humidity at 82° F. (27.8° C.).

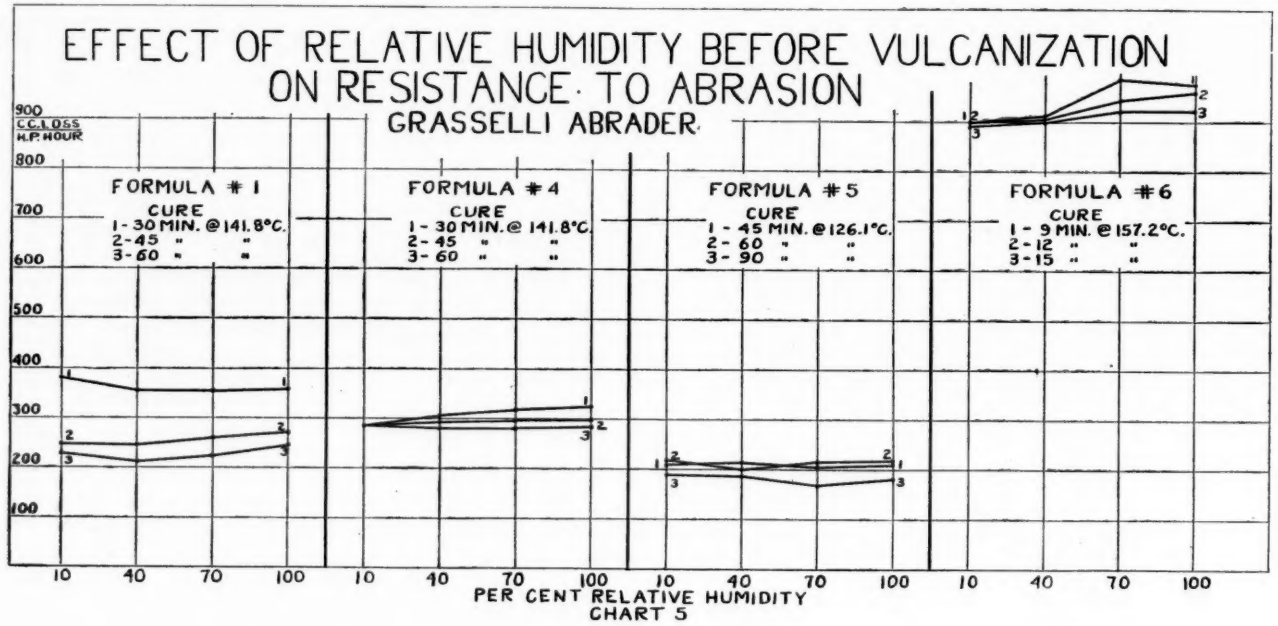
The results are given in Table IV, and the results obtained with the Grasselli abrader, disregarding the power consumption, are given in Table V. The results of the 24-hour exposures are also shown graphically in Charts 4 to 6, inclusive.

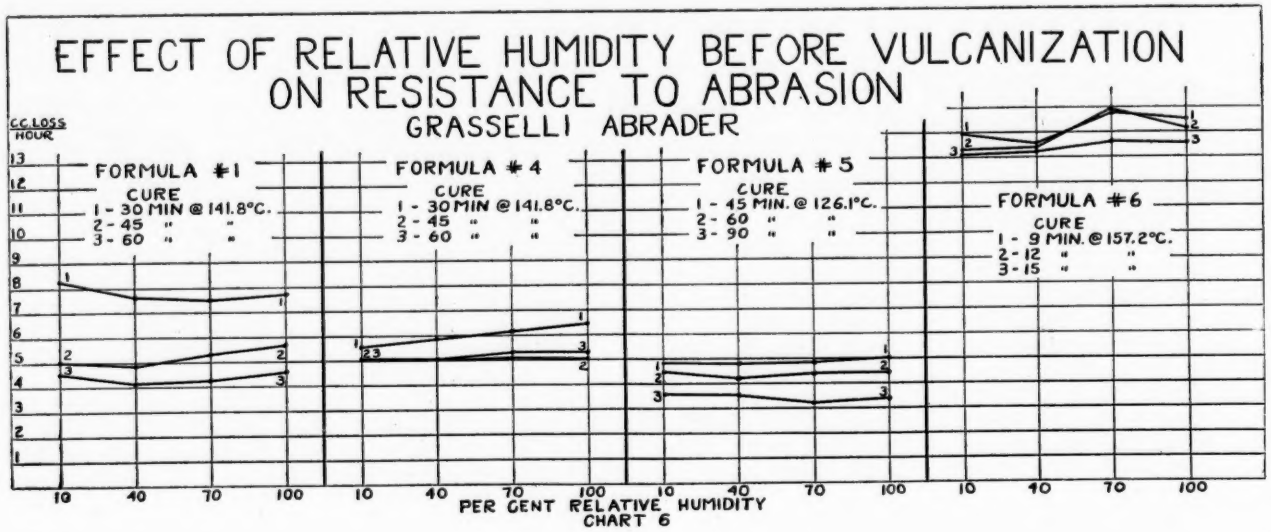
The results show that resistance to abrasion varies but little owing to differences in relative humidity between the mixing and curing. There are slight effects visible in the graphs, but these are rather insignificant and in some cases within the range of experimental error.

Part III—Effect of Varying Temperature while Maintaining Same Relative Humidity during Conditioning of Vulcanized Samples Previous to Testing at 82° F. (27.8° C.)

The cured samples were prepared as heretofore—conditioning the raw stock for 24 hours in an atmosphere of 45 per cent relative humidity at 82° F. (27.8° C.), before vulcanization. Previous to testing at 82° F. (27.8° C.) each of the cures of each stock was conditioned for 24 hours in an atmosphere of 45 per cent relative humidity at each of the three temperatures, 59° F. (15° C.), 82° F. (27.8° C.), and 95° C. In addition, the middle cures of each of the stocks were conditioned for 48 and 72 hours under the same conditions to determine the effect of length of exposure. This relative humidity at the various temperatures may be expressed in terms of absolute humidity (water per liter dry air) thus:


EFFECT OF RELATIVE HUMIDITY BEFORE VULCANIZATION
ON RESISTANCE TO ABRASION
U.S. ABRADER
CC LOSS / HOUR
FORMULA #1
CURE
1 - 30 MIN @ 141.8°C.
2 - 45 " "
3 - 60 " "
FORMULA #4
CURE
1 - 30 MIN. @ 141.8°C.
2 - 45 " "
3 - 60 " "
FORMULA #5
CURE
1 - 45 MIN. @ 126.1°C.
2 - 60 " "
3 - 90 " "
FORMULA #6
CURE
1 - 9 MIN. @ 157.2°C.
2 - 12 " "
3 - 15 " "
12
11
10
9
8
7
6
5
4
3
2
1
10 40 70 100
PER CENT RELATIVE HUMIDITY
CHART 4


EFFECT OF RELATIVE HUMIDITY BEFORE VULCANIZATION
ON RESISTANCE TO ABRASION
GRASSELLI ABRADER
CC. LOSS H.P. HOUR
900
800
700
600
500
400
300
200
100
FORMULA # 1
CURE
1 - 30 MIN. @ 141.8°C.
2 - 45 " "
3 - 60 " "
FORMULA # 4
CURE
1 - 30 MIN. @ 141.8°C.
2 - 45 " "
3 - 60 " "
FORMULA # 5
CURE
1 - 45 MIN. @ 126.1°C.
2 - 60 " "
3 - 90 " "
FORMULA # 6
CURE
1 - 9 MIN. @ 157.2°C.
2 - 12 " "
3 - 15 " "
10 40 70 100
PER CENT RELATIVE HUMIDITY
CHART 5


EFFECT OF RELATIVE HUMIDITY BEFORE VULCANIZATION ON RESISTANCE TO ABRASION
GRASSELLI ABRADER
CC LOSS / HOUR
FORMULA #1
CURE
1 - 30 MIN @ 141.8°C.
2 - 45 " "
3 - 60 " "
FORMULA # 4
CURE
1 - 30 MIN @ 141.8°C.
2 - 45 " "
3 - 60 " "
FORMULA # 5
CURE
1 - 45 MIN. @ 126.1°C.
2 - 60 " "
3 - 90 " "
FORMULA #6
CURE
1 - 9 MIN. @ 157.2°C.
2 - 12 " "
3 - 15 " "
13
12
11
10
9
8
7
6
5
4
3
2
1
10
40
70
100
PER CENT RELATIVE HUMIDITY
CHART 6

° C.	Gram
15	0.0058
27.8	0.0124
35	0.0183

The results are given in Table VII (Charts 7 and 8). Disregarding the power consumption and calculating the values in volume loss per hour, the results obtained with the Grasselli abrader are given in Table VII (Chart 9).

There was little variation in resistance to abrasion due to temperature of storing the cured stock while maintaining the same relative humidity of 45 per cent. Stock 4 with the Grasselli abrader and stock 1 with the U. S. abrader do show a slight trend with the temperature but this is so slight that it may be ignored.

Remarks

In this investigation study of the effect of humidity during testing was omitted in the belief that during such a short time the humidity could not have an appreciable effect. Furthermore, there is a rise in temperature at the surface being abraded, which would make it very difficult to control the humidity. While the tests were being made a record of the relative humidity of the cabinet was kept, but this seemed to make no discernible difference in the results. The relative humidity of the cabinet varied over a considerable range (from 18 per cent to 68 per cent) during these tests, but any differences observed varied in direction and, since it is within the range of experimental error, may be ignored.

Table IV—Resistance to Abrasion as Effected by Exposure of Samples, between Mixing and Vulcanization, to Air of Different Relative Humidities

(U. S. abrader, expressed in cubic centimeters loss per hour; Grasselli abrader, expressed in cubic centimeters loss per horsepower-hour)

Stock	Time Conditioned before Curing		U. S. Abrader at Relative Humidity of:				Grasselli Abrader at Relative Humidity of:			
			10%	40%	70%	100%	10%	40%	70%	100%
	Hours	*Min.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
		At 141.8° C.								
1	24	20	6.01	6.03	5.64	5.60	380	357	359	382
	24	45	4.30	4.38	4.39	4.02	249	245	262	271
	48	45	4.29	4.39	4.33	3.94	247	246	266	272
	72	45	4.29	4.38	4.35	3.90	247	250	261	273
	24	60	4.36	4.35	4.32	3.49	228	213	224	422
4	24	30	4.89	4.53	3.77	4.35	287	303	318	324
	24	45	4.30	4.23	4.31	3.93	284	284	286	284
	48	45	4.17	3.97	4.15	3.94	287	282	282	282
	72	45	4.20	4.04	4.19	3.92	286	285	283	282
	24	60	3.77	3.74	3.75	3.62	285	290	296	303
		At 126.1° C.								
5	24	45	3.89	3.83	3.82	3.61	210	210	208	211
	24	60	2.98	2.89	2.78	2.68	217	204	213	218
	48	60	2.76	2.79	2.92	2.65	222	198	187	183
	72	60	2.72	2.85	2.75	2.63	219	197	186	184
	24	90	2.53	2.67	2.64	2.37	188	185	168	180
		At 157.2° C.								
6	24	9	13.30	11.37	10.99	10.58	898	907	988	973
	24	12	11.06	10.99	10.81	10.43	898	908	941	959
	48	12	10.97	10.97	10.91	10.44	876	917	910	954
	72	12	10.93	10.95	10.78	10.43	878	921	933	954
	24	15	10.04	9.63	9.57	9.54	890	903	921	921

EFFECT OF TEMPERATURE WITH 45% RELATIVE HUMIDITY AFTER VULCANIZATION ON RESISTANCE TO ABRASION

U.S. ABRADER
TESTED AT 27.8°C.

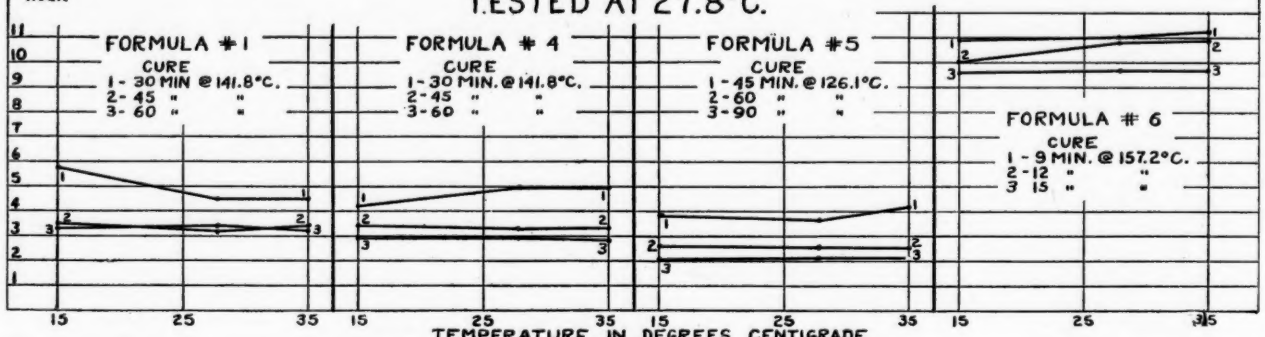


CHART 7

EFFECT OF TEMPERATURE WITH 45% RELATIVE HUMIDITY AFTER VULCANIZATION ON RESISTANCE TO ABRASION

GRASSELLI ABRADER
TESTED AT 27.8°C.

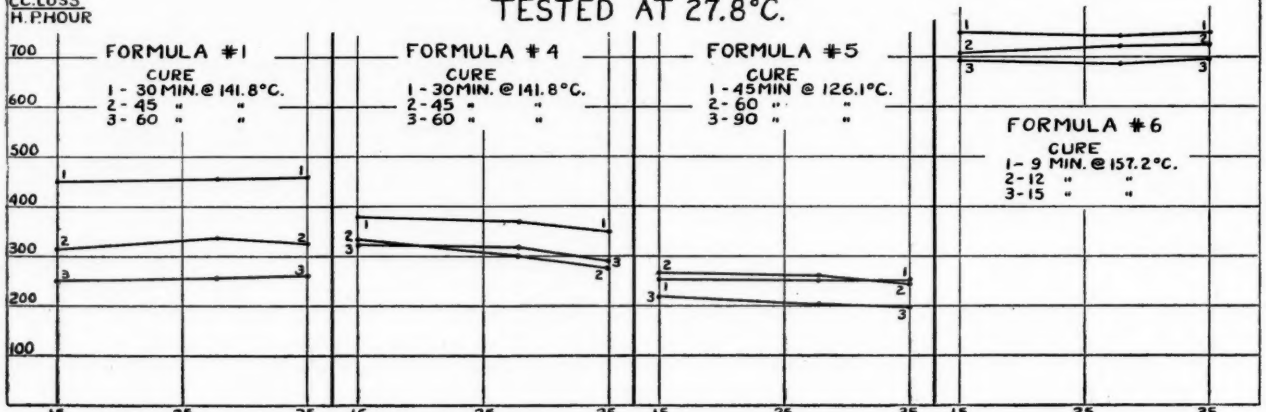


CHART 8

EFFECT OF TEMPERATURE WITH 45% RELATIVE HUMIDITY AFTER VULCANIZATION ON RESISTANCE TO ABRASION

GRASSELLI ABRADER
TESTED AT 27.8°C.

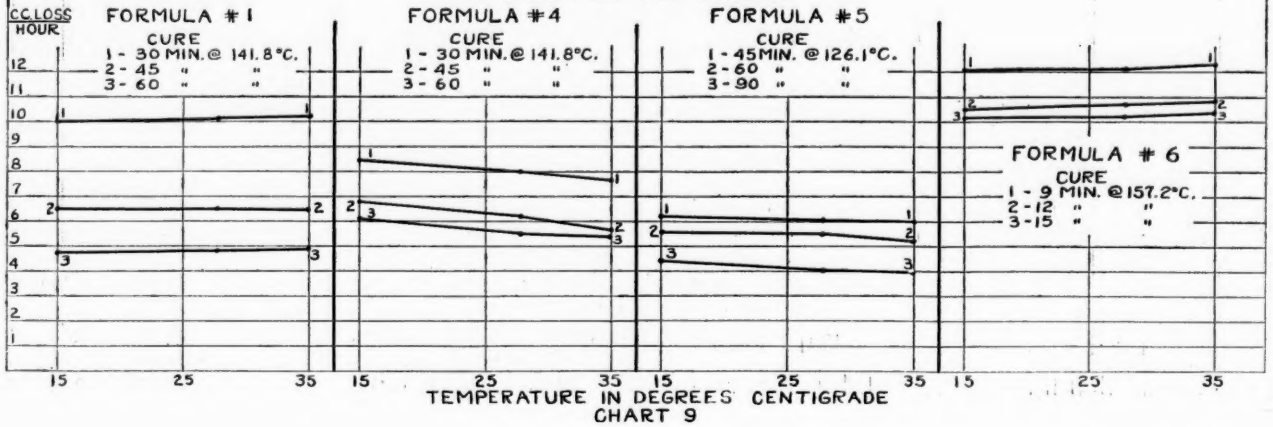


CHART 9

Table V—Resistance to Abrasion (Grasselli Abrader) as Effected by Exposure of Samples, between Mixing and Vulcanization, to Air of Different Relative Humidities, Disregarding Power Consumption

(Expressed in cubic centimeters loss per hour)

Stock	Time Conditioned before Curing		Relative Humidity			
			10%	40%	70%	100%
	Hours	*Min.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
		At 141.8° C.				
1	24	30	8.21	7.56	7.47	7.83
	24	45	4.96	4.84	5.32	5.61
	48	45	4.96	4.86	5.32	5.64
	72	45	4.95	4.99	5.36	5.64
	24	60	4.67	4.14	4.22	4.52
4	24	30	5.58	5.90	6.17	6.47
	24	45	5.08	5.08	5.14	5.07
	48	45	5.13	5.06	5.04	5.05
	72	45	5.12	5.08	5.08	5.06
	24	60	5.07	5.04	5.31	5.25
		At 126.1° C.				
5	24	45	4.79	4.78	4.82	5.02
	24	60	4.50	4.22	4.36	4.44
	48	60	4.54	4.09	3.68	3.61
	72	60	4.48	4.07	3.66	3.62
	24	90	3.58	3.53	3.20	3.43
		At 157.2° C.				
6	24	9	13.93	13.62	14.83	14.60
	24	12	12.30	13.45	14.93	14.20
	48	12	12.96	13.58	13.47	14.12
	72	12	13.00	13.63	13.80	14.12
	24	15	13.17	13.37	13.65	13.64

Table VI—Resistance to Abrasion as Effected by Exposure of Cured Stock to Air of 45 Per Cent Relative Humidity at Different Temperatures

U. S. abrader, expressed in cubic centimeters loss per hour; Grasselli abrader expressed in cubic centimeters loss per horsepower-hour)

Stock	Time Conditioned before Testing		Tested on U. S. Abrader at:			Tested on Grasselli Abrader at:		
			15° C.	27.8° C.	35° C.	15° C.	27.8° C.	35° C.
	Hours	*Min.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
		At 141.8° C.						
1	24	30	5.74	4.51	4.54	450	454	458
	24	45	3.48	3.24	3.41	314	334	327
	48	45	3.84	3.36	3.30	309	326	314
	72	45	3.47	3.34	3.38	310	329	320
	24	60	3.29	3.32	3.29	252	258	262
4	24	30	4.20	4.90	4.87	383	367	349
	24	45	3.36	3.25	3.24	335	301	276
	48	45	3.34	3.23	3.25	333	314	273
	72	45	3.32	3.24	3.26	333	310	276
	24	60	2.89	2.88	2.85	324	311	289
		At 126.1° C.						
5	24	45	3.80	3.70	4.20	256	254	250
	24	60	2.67	2.64	2.47	266	261	247
	48	60	2.65	2.69	2.85	268	263	246
	72	60	2.63	2.62	2.79	270	261	245
	24	90	2.08	2.16	2.18	218	204	197
		At 157.2° C.						
6	24	9	10.87	11.03	11.20	749	744	752
	24	12	10.07	10.83	10.85	708	719	726
	48	12	10.14	10.59	10.81	715	724	734
	72	12	10.16	10.70	10.89	713	723	732
	24	15	9.57	9.65	9.68	692	689	696

Table VII—Resistance to Abrasion (Grasselli Abrader) as Effected by Exposure of Cured Stock to Air of 45 Per Cent Relative Humidity at Different Temperatures, Disregarding Power Consumption

(Expressed in cubic centimeters loss per hour)

Stock	Time Conditioned before Testing	Cure	Tested at:		
			15° C.	27.8° C.	35° C.
	Hours	*Min.*	*Cc.*	*Cc.*	*Cc.*
		At 141.8° C.			
1	24	30	10.04	10.14	10.20
	24	45	6.49	6.59	6.44
	48	45	6.09	6.42	6.18
	72	45	6.12	6.49	6.30
	24	60	4.74	4.86	4.92
4	24	30	8.44	8.07	7.68
	24	45	6.84	6.16	5.64
	48	45	6.81	6.41	5.58
	72	45	6.80	6.33	5.63
	24	60	6.09	5.48	5.45
		At 126.1° C.			
5	24	45	6.14	6.09	6.01
	24	60	5.59	5.47	5.19
	48	60	5.64	5.52	5.17
	72	60	5.58	5.49	5.15
	24	90	4.35	4.08	3.94
		At 157.2° C.			
6	24	9	12.18	12.10	12.23
	24	12	10.48	10.64	10.76
	48	12	10.58	10.72	10.87
	72	12	10.56	10.70	10.84
	24	15	10.24	10.22	10.30

Conclusions

This study shows that in determining resistance to abrasion the temperature of the room or cabinet should be controlled within ±1° C. in order to avoid significant errors in the results from this source. Below are shown the percentage differences per degree Centigrade obtained with each of the stocks. It must be remembered that this probably holds only over the range of temperatures studied and might change rapidly outside of this range. As the temperature changes from 15° C. to 35° C., the resistance to abrasion changes per degree Centigrade in the following manner:

Stock	U. S. Abrader	Grasselli Abrader
	Per cent	*Per cent*
1	+1.25	+1.40
4	+0.40	+0.8
5	+0.60	+0.1
6	−1.8	−0.8

In the light of the present investigation there will be no great error in results caused by differences in relative humidity either with the raw or vulcanized stock. Where laboratories are equipped to condition raw and vulcanized stock for stress-strain tests, it appears that it would be advisable also to condition samples for determining resistance to abrasion. It would at least tend to produce more nearly uniform results by eliminating possible sources of small errors. As the relative humidity during exposure of raw stock increases from 10 per cent to 100 per cent,

the resistance to abrasion per 1 per cent relative humidity changes roughly in the following manner:

Stock	U. S. Abrader	Grasselli Abrader
	Per cent	*Per cent*
1	+0.055	−0.03
4	+0.09	−0.03
5	+0.09	−0.01
6	+0.04	−0.067

As these variations are small compared with the experimental error, it is evident that if the relative humidity does not vary over too wide a range its effect may be neglected.

The temperature of storing the cured samples while maintaining a constant relative humidity has a negligible effect as in the case of relative humidity. As the temperature increases the resistance to abrasion per degree changes in the following manner:

Stock	U. S. Abrader	Grasselli Abrader
	Per cent	*Per cent*
1	+0.125	−0.15
4	−0.3	−0.15
5	−0.4	+0.15
6	−0.025	−0.03

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